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Characterization of Manganese Oxide Coated Filter Media

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A Master's Project Presented By

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Special thanks to my friends, and my family – the best teachers of all. "Without love in the dream it will never come true."

Abstract

Several methods for removal of soluble manganese from drinking water exist. One of these options involves adsorption of the manganese onto Mn oxide coated filter media. Dissolved manganese (Mn(II)) is adsorbed to sites on the Mn oxide coating and then oxidized by free chlorine, thus regenerating the media sites for further Mn adsorption. This method has been successfully used by numerous water treatment plants, decreasing Mn levels to below treatment goals. A disadvantage to this method is the use of chlorine prior to filtration, which can lead to increased levels of disinfection by-products as compared to post-filter chlorination.

Nine plants that use oxide coated filter media for Mn removal participated in this study. The objective of this research was to characterize the filter media at these plants. The media was characterized with respect to size, oxide coating level, surface area and Mn uptake capacity. Laboratory and full scale studies were conducted to assess the impact of changes in pre-filter chlorination on the Mn adsorption process.

The anthracite and sand media from nine drinking water treatment plants had a wide range of oxide coating levels, ranging from less than 0.01 to more than 120 mg Mn per gram of media. All dual media filters show a depth profile with more oxidized Mn on the surface of the media in the upper anthracite layers than in the lower sand layers. Filters with homogeneous media showed no such depth variable profile. The effective size of anthracite media analyzed ranged from 0.67 mm to 1.0 mm. The effective size of sand media ranged from 0.40 to 0.73 mm.

Samples were analyzed for Mn uptake in a recirculating laboratory batch system before and after regeneration with a 20 mg/L solution of free-chlorine for 15-24 hours. Media in the laboratory regenerated state had approximately 130% of the Mn uptake exhibited by media in the as-is (un-regenerated) condition for cases where media had been exposed to continuous pre-filter chlorination at the full scale plants.

The media from the nine plants exhibited a wide range of Mn uptake, ranging from 0.01 to 0.7 mg Mn per gram of media after regeneration (20 mg/L free chlorine). In general, it was found that the Mn uptake by the media was directly proportional to the amount of Mn oxide coating on the media. However, at coating levels above 20 mg Mn per gram of media, an increase in coating level was not found to always yield a proportional increase in Mn uptake.

The surface area of oxide coated filter media was also characterized. Media with Mn coating levels ranging from less than 0.5 to over 120 mg Mn per gram of media had surface areas of 1.2 to 92 m^2/gram of media. Results show that the surface area of media is directly proportional to the amount of Mn oxide coating on the media for traditional media filters. However, samples taken from Mn removal filters that have a particle filtration step upstream in the treatment process had relatively low surface area despite high levels of Mn oxide coating.

Laboratory and full scale studies were conducted to determine the impact of restarting pre-filter chlorination after a period of months when the filter did not receive pre-filter chlorine. Media from the Stamford water treatment plant, which had its Mn uptake capacity exhausted, was shown to resume Mn removal soon after receiving a chlorine dose of 2.0 mg/L. At the full-scale, after a period of 5 months without chlorine, the oxide coated media produced satisfactory Mn effluent concentrations upon resumption of pre-filter chlorination.

These results indicate that the characteristics of oxide coated filter media and the process of Mn adsorption are interdependent. A sound understanding of the filter media at a particular water treatment plant could facilitate an optimization of the Mn adsorption process. Further research is recommended to better understand the contribution of particles encapsulated in Mn oxide coating to the surface area of the filter media.

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1.0 Introduction

1.1 Problem Statement

High levels of manganese (Mn) can cause drinking water quality and drinking water distribution system problems. Dissolved Mn can become oxidized and lead to discolored water as well as staining of surfaces and laundry in the home. It can also cause problems by depositing on the pipes of a water distribution system. Due to these aesthetic problems, the USEPA issued a secondary maximum contaminant limit (SMCL) of 0.05 mg/L for Mn (USEPA, 1979).

In water, Mn can exist in several oxidation states. Dissolved Mn is in the reduced form, Mn(II) which has an oxidation state of +2. Mn also exists in two oxidized, insoluble forms, Mn(III) and Mn(IV). Mn can also exist in an oxidant form, Mn(VII), commonly occurring as permanganate, MnO_4^-.

This study focuses on Mn removal in drinking water treatment systems which use surface water sources. In surface water systems, there are several potential sources of Mn. During periods of lake and reservoir stratification Mn can be reduced in an anoxic hypolimnion. As the water body turns over, seasonally, and mixes, the reduced and dissolved Mn can readily enter the treatment system. There are also sources of Mn within a treatment plant. Particulate Mn in solid residuals can be reduced should the residuals become anoxic, dissolving the Mn. Mn can also be present as a contaminant in ferric coagulants.

One method for removal of Mn is adsorption of the dissolved Mn onto an oxide surface and then subsequent oxidation of the adsorbed Mn with an oxidant. After the dissolved Mn is adsorbed and oxidized, the surface sites for adsorption are regenerated, allowing for more adsorption. It is common for this process to occur on filter media if chlorine is present during the filtration of water that contains dissolved Mn. This process is commonly referred to as the natural greensand effect. The primary disadvantage of this process is the potential for increased disinfection by-product (DBP) formation. The addition of chlorine prior to water filtration has been demonstrated to increase DBP formation (Corbin *et al.*, 2003) as compared to post-filter chlorination. Thus removal of Mn via adsorption to oxide coated filter media requires a balancing and optimization of the removal process while minimizing DBP formation.

This M.S. Report is part of a larger study of Mn removal by oxide coated media, funded by the American Water Works Association Research Foundation (AwwaRF, Project number – 2951) and the Aquarion Water Company of Connecticut (AWC), with participation by several other utilities. The ultimate objective of the study is to increase fundamental and practical knowledge regarding the use of adsorption by oxide surfaces for control of Mn in treated drinking waters. This report focuses on the characterization of oxide coated filter media from a range of surface water treatment plants.

1.2 Research Objectives

The main objectives of this research were to:

1. Characterize oxide coated filter media with respect to size, amount and ratios of existence of metals in surface coatings (Mn, Fe, Al) surface area, metal ratios and Mn adsorption capacity.
2. Evaluate the effectiveness of different media and treatment processes for soluble Mn removal.

1.3 Scope of Work

The project involved field sampling, laboratory experiments and analysis of field data and experimental results. Raw water and treatment process data were obtained for each treatment plant and analyzed. Field sampling was performed at participating plants to collected filter media. Laboratory experiments and analyses were performed to characterize the size, metal coating levels, surface area and adsorption capacity of the media. Full-scale, pre-filter chlorination experiments were conducted at the Warner treatment plant. During this period, an analysis of raw and filtered Mn levels was conducted.

2.0 Background

This chapter is a review of some of the published research pertaining to manganese and its removal in drinking water treatment systems. The chapter is divided into several separate parts. Section 2.1 focuses on the problems caused by manganese, both health and aesthetic. Section 2.2 contains information pertaining to manganese regulation. Sections 2.3 and 2.4 summarize the fundamentals of manganese chemistry and its sources in water. Sections 2.5 and 2.6 summarize research done on different manganese removal methods including adsorption onto oxide coated filter media. Finally, section 2.7 focuses on the characterization of metal oxide coated media.

2.1 Manganese Problems

In drinking water, manganese can operational and aesthetic problems, while the potential for adverse health effects is very limited.

2.1.1 Health Effects of Manganese

Manganese is a transition metal, ubiquitous in the environment. 0.1 percent by mass of the earth's crust is comprised of manganese (Griffin, 1960). Manganese is an essential nutrient to human growth. The Food and Drug Administration (FDA) recommends a daily intake of 2 mg of manganese per day (FDA, 2006). However, in high concentrations, manganese could cause adverse health effects, which have been well documented. The Agency for Toxic Substances and Disease Registry (ATSR) published a toxicological profile for manganese (ATSR, 2000). The report states that the primary pathway for human expose to manganese is through inhalation and that there are no significant toxic effects of manganese exposure through the ingestion of food or water. Exposure to high concentrations of manganese has been shown to affect the central nervous systems. Chronic exposure can cause slower reaction time, poor hand steadiness and impaired hand eye coordination (USEPA, 2006). Manganese has not been found to be carcinogenic. The USEPA recommends a reference dose (RfD) of 10 mg/day (USEPA, 2006). At typical concentrations in drinking water, the health effects from manganese exposure in drinking water are negligible.

2.1.2 Aesthetic and Operational Problems

In drinking water treatment, aesthetic and operational problems are caused when dissolved, reduced Mn(II), usually present as Mn^{+2}, is oxidized to form MnO_2 solid which has a black color. When oxidation occurs in a water distribution system, scaling can develop on pipes. Sly et al. (1990) found two different processes leading to manganese oxidation. Where chlorine was present, manganese was oxidized on the surface of the distribution pipes. Where chlorine was not present, manganese oxidizing bacteria were able to oxidize the manganese and also form a biofilm on the pipe walls. Sloughing off of the coating and biofilm caused aesthetic problems. Increasing amounts of coating and biofilm were also found to restrict pipe flow. Sly et al. recommended that water treatment plants produce effluent with a maximum Mn concentration of 0.01 mg/L. When oxidation occurs in a consumer's home, it can lead to discolored water, and also staining of surfaces and laundry. At concentrations greater than 0.2 mg/L, manganese can also cause taste and odor complaints.

2.2 *Drinking Water Regulations*

As part of the regulation of drinking water, the USEPA issues two general types of drinking water regulations: primary and secondary standards. Primary standards are enforceable standards for contaminants that pose a health risk to consumers. Secondary standards are reserved for contaminants which cause aesthetic problems but do not pose a health risk. Secondary standards are not enforceable. The USEPA regulates manganese through a secondary maximum contaminant level (SMCL) of 0.05 mg/L which resulted from the Safe Drinking Water Act of 1974.

The USEPA places contaminants that might be best regulated by primary standards on a Contaminant Candidate List (CCL). Manganese was placed on the CCL in 1998 while it was determined if it would best serve public health if it was regulated by a primary standard. An examination of current toxicological data from the ASTDR showed that the health risks associated with exposure to manganese in drinking water would not be further reduced by regulating Mn by a primary standard. Thus, manganese remains regulated by a SMCL and was removed from the CCL (USEPA, 2003).

2.3 Manganese Chemistry

2.3.1 Redox Chemistry and Complexation

The most commonly found oxidation state of dissolved manganese in water is Mn(II). This reduced form is relatively soluble in water and exists as $Mn^{+2}(aq)$. Mn(III) and Mn(IV) are two of the more oxidized states of manganese; both forms are highly insoluble in water and occur as $MnOOH(s)$ and $MnO_2(s)$ respectively. A mixed oxidation state of manganese can also occur, referred to as MnO_x, where x ranges from 1.3 to 2.0 (Morgan and Stumm, 1964). Manganese can also exist as Mn(VII), occurring as MnO_4^-, permanganate, which is an oxidant that is used in water treatment.

Dissolved manganese can form several complexes with inorganic anions. Mn^{+2} complexes with carbonate at a pH greater than 7.5, assuming an adequate concentration of carbonate. Mn^{+2} can also form a complex with the hydroxide anion at a pH greater than 11.5. For most pH values applicable to water treatment, 6 to 7.5, dissolved manganese exists primarily as Mn^{+2}.

2.3.2 Manganese Fractionation

Oxidized manganese can be a solid in two different size categories: colloidal and particulate. Colloidal manganese oxide particles are significantly smaller than particulate manganese (Carlson et al. 1997). A common pore diameter for standard separation of particulate versus dissolved manganese is 0.45 μm. However, oxidized manganese can exist in a wide range of sizes and more filtration steps are required to differentiate between colloidal and particulate manganese (De Vitre et al., 1998).

A large amount of oxidized, colloidal manganese from surface water was found to pass through a filter with an effective diameter of 0.45 μm (Lazerte and Burling, 1990). To separately identify colloidal versus particulate manganese, differential pulse anodic stripping voltammetery (DPASV) was used. However, some irregular results were obtained from the DPASV. The authors concluded that high concentrations of dissolved organic carbon (DOC) were complexing with the manganese and inhibiting the test.

Building on the work of Lazerte and Burling (1990), a multi-step filtration separation approach to determine manganese fractionalization was developed by Carlson et al. (1997). The authors used a 0.2 μm filter to differentiate between particulate and dissolved plus colloidal manganese and also a 30,000 apparent molecular weight (amw) membrane ultrafilter to differentiate between colloidal and dissolved Mn.

2.4 Sources of Manganese in Surface Waters

In a surface water body, manganese can exist in the particulate, colloidal and dissolved forms. During periods of lake stratification, an anoxic hypolimnion and an aerobic epilimnion can form. In the aerobic epilimnion, the oxidizing environments caused by the higher dissolved oxygen (DO) layer and aerobic microbial metabolism can lead to oxidation of dissolved Mn which precipitates and settles to the hypolimnion. The reducing conditions in the low DO hypolimnion layer and microbial metabolism can lead to the reduction of colloidal and particulate manganese to Mn(II), increasing levels of dissolved Mn^{+2}. In the late summer or early fall, many lakes experience a period of turnover, and the contents of the lake are in that case mixed (Lechevallier et al. 2002).

The form and concentration of manganese entering a treatment plant can vary with the time of year. A surface water body in Fort Collins, Colorado was found to have low Mn concentrations during most of the year with an acute increase in manganese concentration during the late summer and early fall (Carlson et al., 1997). This pattern is seen in many bodies of water the northern hemisphere. In the late summer, the authors reported that the Mn was almost exclusively in the dissolved form, and in the remaining months the majority of the Mn entering the plant was particulate.

2.5 *Manganese Removal by Direct Oxidation*

When manganese enters a water treatment plant in the dissolved Mn(II) form there are several options for removal. Manganese removal by oxidation has been commonly used by water treatment utilities. In removal by oxidation, dissolved Mn(II) is oxidized to Mn(IV) forming the solid $MnO_2(s)$, as seen in Equation 2-1.

$$Mn^{+2}(aq) + oxidant \rightarrow MnO_2(s) \qquad \textbf{Equation 2-1}$$

The solid $MnO_2(s)$ is removed in the clarification and filtration processes of treatment. Strong oxidants are typically used in this removal process, including permanganate, chlorine dioxide and ozone.

2.5.1 Oxidation with Free Chlorine

Knocke et al. (1987; 1991) investigated the kinetics of manganese oxidation using several oxidants, including free chlorine. The stoichiometric dose for oxidation of Mn(II) to Mn(IV) by free chlorine is 1.30 mg Cl_2 per mg Mn^{+2}. However, Knocke et al. found that a much higher dose than predicted by stoichiometry was required for Mn oxidation. The authors state that this was most likely due to demands for the chlorine in water. The rate of oxidation of manganese with free chlorine was found to be slow; over one hour of contact time was needed for oxidation at pH values typical of water treatment. The oxidation was also found by the authors to be slowed further by temperatures below 41 deg F. Therefore, free chlorine is not a good oxidant choice for direct Mn oxidation. However, slow oxidation by free chlorine will occur in water distribution systems due to long contact time.

2.5.2 Oxidation with Permanganate

Knocke et al. (1987;1991) also researched the oxidation of manganese using potassium permanganate, $KMnO_4$. The stoichiometric dose for oxidation of manganese from Mn(II) to Mn(IV) is 1.92 mg $KMnO_4$ per mg Mn^{+2}. The oxidation of Mn(II) with $KMnO_4$ was found to be very rapid, occurring in one minute or less for pH values typically used in drinking water treatment. The rate of oxidation was found to increase with increasing pH. The rate of the reaction was found to be slowed by low temperatures and demand for the permanganate by reaction with organic matter. The authors state that this organic demand for the permanganate must be met before Mn oxidation can occur. When an excessive amount of permanganate was added for oxidation, the dissolved manganese concentration was shown to increase. The authors concluded that oxidation of manganese using permanganate is effective and viable for water treatment assuming that the dose of permanganate is optimized. Gregory and Carlson (2003) also studied oxidation of manganese with permanganate. They found that oxidation took over 30 minutes, much longer than reported by Knocke et al. Gregory and Carlson used raw water with a lower concentration of manganese than Knocke et al, (60 μg/L and 200 μg/L versus 1.0 mg/L) and were also attempting to decrease the soluble manganese to a lower level (10 μg/L versus approximately 100 μg/L).

2.5.3 Oxidation with Chlorine Dioxide

The oxidation of manganese with chlorine dioxide was also studied by Knocke et al. (1987, 1991). The stoichiometric dose for oxidation of Mn(II) to Mn(IV) is 2.45 mg ClO_2 per mg of Mn^{+2}. Oxidation by ClO_2 occurred relatively rapidly, however over twice the stoichiometric dose was required to achieve full oxidation. The rate of oxidation was pH dependent, increasing as pH increased. Gregory and Carlson (2003) determined that chlorine dioxide was the most effective oxidant for manganese removal at the Horsetooth Reservoir which has an average total organic carbon (TOC) concentration of 3.5 mg/L. For this water, ClO_2 was able to oxidize Mn so that it was removed to a level below 10 μg/L in less than two minutes. The rate of oxidation with ClO_2 was faster than for any of the other oxidants studied (permanganate, ozone and chlorine). Also, the reaction between Mn^{+2} and ClO_2 did not produce permanganate, as occurred for oxidation using ozone. There are, however, undesirable by-products of oxidation with ClO_2. Chlorate and chlorite, which are regulated by the EPA, are both formed by the reduction of ClO_2.

2.5.4 Oxidation with Ozone

Gregory and Carlson (2001;2003) also studied ozone as an oxidant for manganese removal. The rates of reaction between O_3 and Mn^{+2} were observed to be rapid, however the final Mn^{+2} concentrations were higher than desired (>10 μg/L). The stoichiometric dose for oxidation of Mn(II) to Mn(IV) is 0.87 mg O_3 per mg of Mn^{+2}. There is also a demand for O_3 exerted by natural organic matter (NOM) (Wilczak et al., 1993). Gregory and Carlson (2003) state that an O_3 dose must be optimized to meet demand without dosing with an excessive amount of O_3 which can lead to the formation of permanganate (Mn(VII)).

2.5.5 Oxidized Manganese Removal

Oxidized particulate manganese can be destabilized through coagulation and subsequently removed through clarification and granular media or membrane filtration. Particulate manganese can also be removed by membrane filtration without coagulation. This method for removal is typically practiced in groundwater with low NOM content.

The majority of manganese that exists in nature is found in the oxidized, particulate form Carlson et al. 1997). Oxidation of Mn(II) with strong oxidants can lead to manganese in the colloidal size range which may be difficult to destabilize and remove effectively using traditional media filtration (Knocke et al., 1991).

For colloidal sized manganese, membrane filtration has proved to be effective (Baldwin and Jacobsen (2003)). In this study, groundwater was treated with the pre-oxidant $KMnO_4$ and then filtered using parallel membrane, greensand and dual media filters. The membrane process was a hollow fiber, "outside-in", low pressure, ultra-filtration process by Zenon Environmental, Inc. The membrane process outperformed the other forms of filtration and was selected as the process of choice based on the pilot testing results. Neither the greensand nor the dual media was shown to meet the manganese treatment goal of 0.03 mg/L effectively.

2.6 *Soluble Manganese Removal via Adsorption and Oxidation*

Dissolved manganese can also be removed by adsorption onto metal oxide coated filter media. This method has proven to be an effective alternative to oxidation and subsequent filtration of particulate manganese. In this process, granular filter media is covered in a manganese oxide coating with chemically adsorbs Mn^{+2} and then acts as a catalyst for subsequent oxidation of the Mn^{+2} on the oxide surface by chlorine. The oxidation of the adsorbed Mn^{+2} regenerates the adsorption sites and creates additional oxide coating. Griffin (1960) first studied the phenomena and reported that constant application of water with manganese and chlorine to a filter caused sand grains to become black.

The following equations describe the process of manganese adsorption and oxidation (Adapted from MHW, 2005):

$$Mn^{+2}(aq) + MnO_2(s) \rightarrow Mn^{+2} \bullet MnO_2(s) \qquad \textbf{Equation 2-2}$$

$$Mn^{+2} \bullet MnO_2(s) + oxidant \rightarrow 2MnO_2(s) \qquad \textbf{Equation 2-3}$$

2.6.1 Manganese Adsorption

Morgan and Stumm (1964) reported on the sorption of Mn^{+2} cations to MnO_2 solid after running several alkalimetric titrations of a MnO_2 suspension. Addition of Mn^{+2} cations to the MnO_2 suspensions lead to a positive displacement of the titration curves which was concluded as resulting from the exchange of Mn^{+2} for H^+ in the solid phase. The capacity of adsorption was found to increase with increasing pH. At a pH value of above 9, adsorption was inhibited by partial air oxidation of the Mn(II). Figure 2-1 is a plot of Mn(II) adsorption per mole of manganese oxide for varying pH values. At pH 7 the adsorption capacity of manganese oxide was found to be approximately 0.3 mol Mn^{+2} per mol of MnO_2. At pH 7.5 the adsorption capacity had increased to 0.5 mol Mn^{+2} per mol MnO_2.

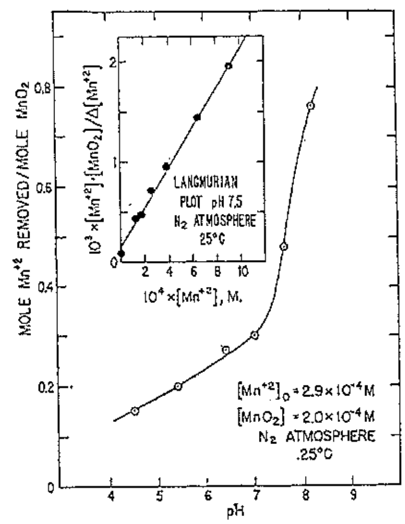

Figure 2-1 pH dependent sorption of Mn(II) on Manganese Dioxide (Morgan and Stumm, 1964)

2.6.2 Procedure for Creating Oxide Coating

An Mn oxide coating can develop gradually on traditional filter media (anthracite and sand) if the media is exposed to dissolved Mn^{+2} and chlorine. Manganese oxide can also be engineered to form on media. Knocke et al. (1990) published a full-scale procedure for developing an Mn oxide coating on filter media. The procedure calls for backwashing the filter, then filling it with a 100 mg/L solution of potassium permanganate and 100 mg/L of chlorine. Sodium hydroxide may also be added to raise the pH to above 6, if necessary. After dosing, the filter needs to stand with the solution for 24 hours, and then operated in a filter-to waste mode to remove the excess potassium permanganate and chlorine. The procedure then calls for the filter to be backwashed again. After backwashing, the authors state that the filter should be capable of producing

Mn effluent concentrations of less than 0.05 mg/L, assuming adequate pre-filter chlorination.

Merkle et al. (1997) developed a bench scale procedure for developing a coating on filter media. The two-stage method used a stirred tank reactor (STR) followed by a re-circulating flow fix-bed reactor. In the stirred tank, filter media was mixed in a water with a Mn concentration of over 350 mg/L. Tin was added to the solution to promote the initial adsorption of Mn(II) on the uncoated media. HOCl and bicarbonate were added to the solution at 20, 40, 50 and 60 minutes. An average coating of 0.64 mg Mn per gram of media was found after this step. Media was then taken from the STR and placed in a recirculating flow fix-bed reactor. In this reactor, a 1000 mg/L Mn solution was recirculated through the media, while every 15 minutes a 100 mg/L solution of HOCl was added. An average coating of 2.0 mg Mn per gram of media was seen after this step.

2.6.3 Mn(II) Sorption and Oxidation using Oxide-Coated Filter Media

After a media filter has been coated with manganese oxide, it can be used to adsorb Mn(II). Weng et al. (1986) found improved Mn(II) removal by a pilot plant using oxidation by $KMnO_4$ after new filter media was replaced with aged filter media. HOCl was determined to be a better suited oxidant because it did not oxidize the Mn(II) prior to reaching the filter media as did the $KMnO_4$.

A direct comparison between un-coated and oxide-coated filter media was conducted by Knocke et al. (1988). The authors performed laboratory-scale filtration studies to assess and compare Mn(II) removal by new filter media and coated filter media. The virgin sand and anthracite were found to have no significant Mn(II) removal capacity. However, the presence of oxide coating yielded significant removal. Filter media with greater amounts of oxide coating were found to typically yield acceptable Mn(II) removal for longer periods of time. However, some media with high amounts of MnO_2 coating were found to have poor removal. Further investigation by the authors led to the conclusion that removal was dependent on the oxidation state of the $MnO_x(s)$ coating. The coated media that exhibited poor removal was found to have oxide coating as $MnO_{1.4\text{-}1.6}(s)$ which was significantly less oxidized than the media with good removal, $MnO_{1.8\text{-}2.0}(s)$. A lower oxidation state indicated that most of the manganese on the filter media is in a reduced form, meaning that the adsorption sites may be occupied.

Knocke et al. (1988) noted the dependence of Mn(II) adsorption on filtration pH. When filtration pH was reduced from 8 to 6, adsorption capacity decreased by 80%. The authors state that this could be of importance to treatment plants considering pH reduction for optimized organics removal. pH values of below 6 and above 8 were not tested. A decrease in temperature was found to have no effect on the Mn adsorption process.

In their bench-scale experiments, Knocke et al. (1988) studied the effect of various pre-filter oxidants for continuous generation of oxide coating during Mn(II) adsorption. Cl_2, $KMnO_4$, O_3 and ClO_2 were compared. When Cl_2 was used, Mn(II) removal by adsorption was very efficient. The demand for the Cl_2 was found to be a function of the pre-filter Cl_2 dose. The authors state that this indicates that the Cl_2 added beyond the theoretical stoichiometric ratio was oxidizing the pre-existing oxide coating on the media. The kinetics of adsorption and oxidation were found to be very rapid. Adequate effluent Mn(II) concentrations were produced at filter hydraulic loading rates over 5 gmp/ft^2. When a stronger oxidant was used, 75% to 90% of the applied Mn(II) was oxidized to colloidal MnO_x(s) prior to reaching the filters. Manganese that was removed in this way was done so through filtration, not adsorption. Breakthrough of manganese occurred as a result of the penetration of stable colloidal MnO_x(s) through the filter.

Knocke et al. (1991) conducted lab-scale columns tests with media of varying coating levels to quantify adsorption rate and capacity. The authors found that Mn uptake was directly proportional to coating level. In an experiment at pH 6-6.2 with influent manganese concentration of 1 mg/L, a media with 42 mg Mn per gram of media did not experience manganese breakthrough after treating 200 L of influent. The authors also found that Mn uptake was directly proportional to filtration pH. Three tests were run with increasing pH from 6 to 8.8 on media with an oxide coating of 3 mg Mn per gram media. At a pH of 8.8 there was no breakthrough during the course of the experiment.

Knocke et al. (1991) also conducted lab-scale columns tests with and without pre-filter chlorination. Media with an oxide coating level of 18 mg Mn per gram of media was tested without HOCl and with an HOCl dose of 2.0 mg/L at a pH of 6.2. When pre-filter HOCl was used, the authors reported continuous removal of manganese. Parallel, full-scale experiments showed that the majority of Mn(II) uptake with pre-filter chlorination occurs in the top 6 inches of the filter media.

2.6.4 Modeling Mn(II) Removal by Oxide Coated Filter Media

Coffey et al. (1993) attempted to couple the work of Morgan and Stumm (1964) to field observations made at WTPs to further the understanding of Mn(II) adsorption. Mathematical models were developed by the authors to predict conditions needed for efficient Mn(II) adsorption onto oxide coated media and subsequent media regeneration. The authors developed two separate models, a continuous regeneration model and an intermittent regeneration model. The continuous regeneration model considers influent and effluent manganese concentrations, media depth, pH of filtration, HLR and chlorine dose. The results of the continuous regeneration model can be used to make preliminary design estimations for filter media requirements to produce adequate Mn(II) removal. The intermittent regeneration model is based on a linear adsorption isotherm and first order kinetics. The empirical model can be applied by water treatment plants to predict the breakthrough time for manganese using an oxide coated media filter.

Merkle et al. (1997) developed a process model for soluble Mn(II) removal by oxide coated filter media. The model was based on results of physical and chemical characterization of filter media sampled. A conceptual equation for the model is shown in equation 2-4.

$$Mn^{+2} + Site + HOCl \rightarrow MnO_x(s) + Site \qquad \textbf{Equation 2-4}$$

A continuous regeneration model and an intermediate generation model were constructed. The continuous regeneration model was based on the assumption that dissolved manganese adsorption and oxidation occurs on sites at the surface. The intermediate regeneration model was calibrated by using a fitting parameter to describe the fraction of sites available for adsorption. The model was shown to make better predictions for media with high Mn adsorption capabilities compared to those with lower Mn uptake capabilities. In this study, the authors also found that calcium may be competing with manganese for the adsorption sites. The authors found a hindrance of Mn(II) adsorption at a calcium concentration greater than 60 mg/L.

2.6.5 Manganese Oxide Coating on Filter Media

When adsorbed Mn(II) comes into contact with HOCl, more MnO_x sorption sites are generated. As long as HOCl is allowed to react with the adsorbed Mn(II) the amount of oxide coating on a filter media will increase. However, during filter backwash it is evident that some coating is lost, most likely due to abrasion between grains. Between these too competing processes, the extent to which $MnO_x(s)$ will accumulate on a filter media is not yet well understood.

Hargette and Knocke (2001) studied the fate of manganese in oxide coated filter media, and tried to quantify the affect of filter backwash on the coating. The pilot scale experiment backwashed filters at different rates (15, 22 and 30 gmp/ft^2). In general, increased backwash flow rates yielded greater Mn coating loss. However, backwashing did not in completely remove of the coating, regardless of backwash rate. The authors also found that much more manganese (~50%) was removed from the filter media after operation at a filtration pH 7.3 than backwashing after operation at a filtration pH of 6.0 (10-26%). The authors conclude that this result was caused by some of the Mn(II) being oxidized by HOCl at the higher pH prior to reaching the filters thus causing deposition of colloidal Mn and subsequent removal in backwashing.

The authors also studied the net change in manganese coating over several filter runs at the pilot scale. Filter corings were taken after 3, 6 and 9 filter runs. The filters were operated at a pH of 6.0 and a backwash rate of 15 gpm/ft^2. The influent Mn concentration was 0.3 mg/L. The results, shown in Figure 2-2, demonstrate the gradual build-up of manganese on the filter media through the filter runs. A higher filter backwash rate was found to slightly increase the rate of manganese loss in the filter. Using air scour during backwash was also found to remove more manganese from the media, but only from the top several inches of the filter.

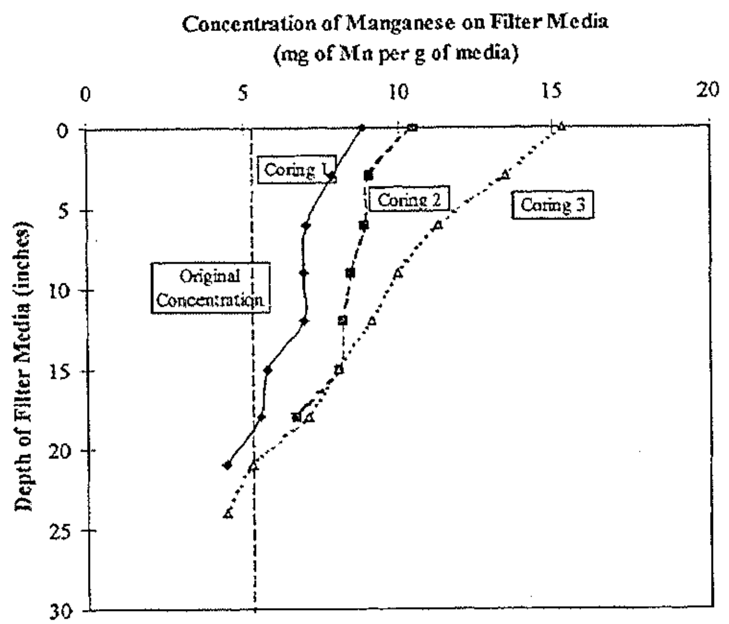

Figure 2-2 Accumulation of Mn Oxide After Filter Runs (Three Filter Runs per Coring)

(From Hargette and Knocke, 2001)

A study by Gabelich et al. (2005) demonstrated release of Mn from a filter media after a treatment plant had changed its treatment process. The Mill Filtration Plant in Riverside, California saw an increase of manganese in the effluent of the treatment plant after switching from pre-filter chlorination to pre-filter ozonation and biological filtration. The Mn release was attributed to removal of Mn coating that had accumulated during years of using pre-filter chlorination and a Mn contaminated ferric chloride coagulant. An attempt to remove the Mn coating by chemically cleaning the media was found to be ineffective. Ultimately a filter media replacement was recommended. The Mn release was found to be increased by the use of a ferric coagulant. This was attributed to the presence of Mn as a contaminant in the iron based coagulant.

2.7 Oxide Coating Characterization

Characterizing filter media mineral coatings is the focus of this report. Several studies have been conducted by various authors to characterize aspects of the coating and ultimately better understand filtration phenomena. These studies used analytical techniques typically used in the geological sciences.

Merkle et al. (1996) studied filter media taken from numerous full-scale water treatment plants. The authors measured the amount of oxide coating on the media as well as the surface area and internal porosity. The studied also included the results of imaging by scanning electron microscopy (SEM).

Figure 2-3 is a cross sectional SEM image of oxide coating on a grain of anthracite (far left in figure). Figure 2-3 shows an alternating pattern of oxide coating. The authors state that this pattern results from an alternation of Al and Mn deposition on the media. The proposed reason for this is seasonal variation in raw water quality at the plant from which the media was taken. In months with low influent Mn, Al from the coagulant is the main source of metal on the filter media. Chemical compositions were confirmed by energy-dispersive X-ray spectrophotometry (EDS).

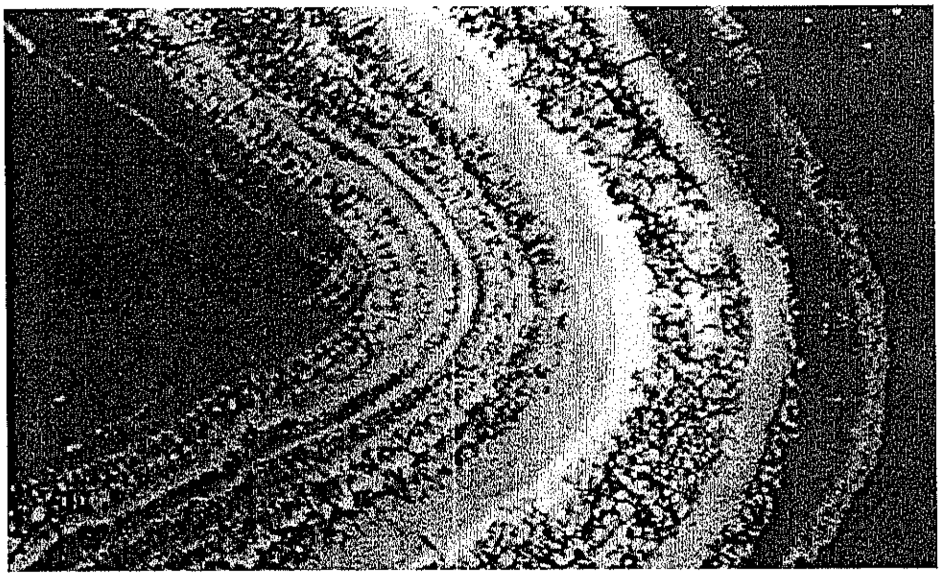

Figure 2-3 SEM Image of Oxide Coating (Merkle et al., 1996)

Merkle et al. (1996) also measured the surface area of oxide coated media and found a linear correlation between measured Mn coating level and surface area. This linear correlation is shown in Figure 2-4. Raw anthracite was found to have a surface area of 0.17 m^2/g media, significantly more than the external surface area assuming a density of 1.59 g/cm and a diameter of 1mm, 0.0038m^2/g. The surface areas for media sampled from all filters followed a linear relationship despite coming from different treatment plants. The authors conclude that the majority of the surface area is associated with micro pores and that only the outermost available sites on the coating will be active in adsorption and site regeneration by oxidation catalysis.

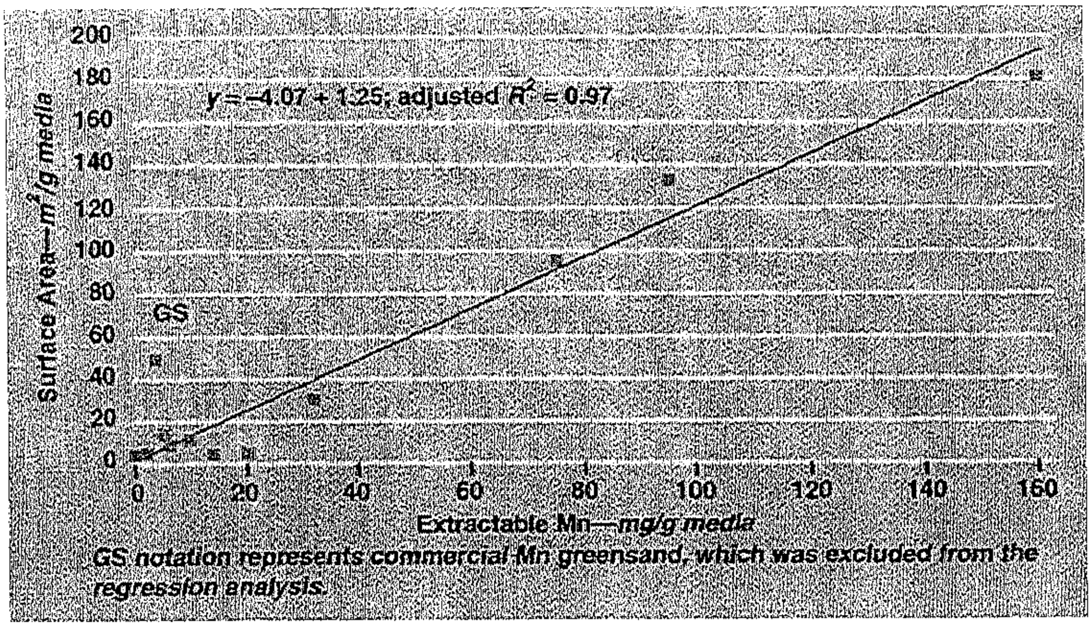

Figure 2-4 Relationship of Media Surface Area and Oxide Coating Level (From Merkle et al. 1996)

Micro pores and surface roughness may also enhance the interception and retention of non-Brownian (submicron) particles by disrupting the laminar sub-layer. The authors state that for all particles the increase in exterior surface area increases the effective collector area for attachment to the media surface. Also, if the surface is undergoing active mineral deposition, particles that may otherwise detach may be encapsulated by coating overgrowth.

The authors also studied the effect of backwashing on the mineral coating of the media. Two SEM (set in backscattered electron mode (BSE)) images of an oxide coated anthracite grain were taken, before and after backwashing. The backwashing was shown to drastically change the surface topography and surface area. Merkle et al. (1996)

conclude that backwashing also affects the external and internal mass transport process and possibly the total sorption capacity for Mn(II). However, the results show that Mn(II) removal processes by oxide coated media can be effective after an entire backwash and filtration cycle.

Hu et al. (2004) also evaluated the characteristics of manganese coated sand using SEM and EDAX analysis. The study was conducted to increase the knowledge base of manganese oxide coatings and better understand and utilize the adsorbent properties of the coating. The results of the EDAX analysis show an interfacial layer co-structure at the interface of the manganese-coating and the sand. The EDAX result is shown in Figure 2-5.

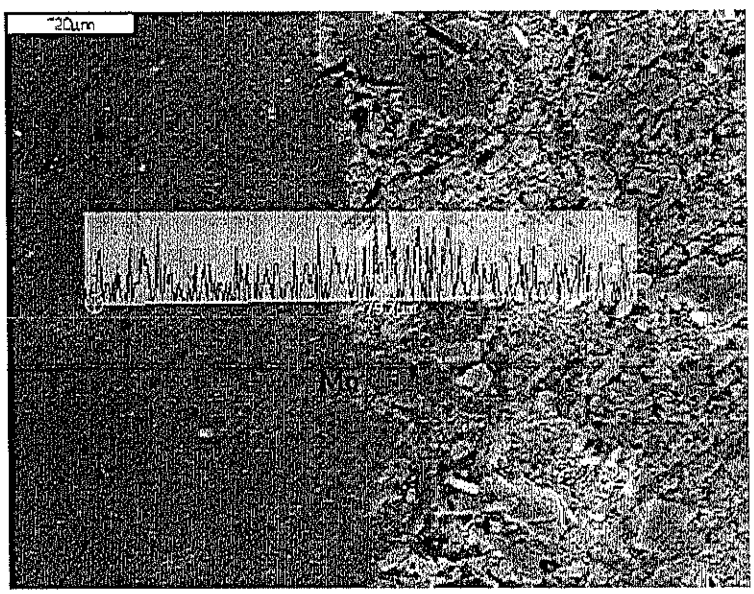

Figure 2-5 Line Scanning of Mn on Cross-Section of Mn Coated Sand (From Hu et al. (2004))

The authors conclude from the SEM/EDAX results that there is diminution of manganese intensity inside of the silica. This indicates a small amount of superficial diffusion of Mn into the sand. The EDAX results also show that compared to the uncoated sand, the manganese coated sand had more micropores and a higher surface area due to the coating.

Hu et al. (2004) also tested the acid and alkali resistance of the manganese oxide coating. The manganese coated sand was placed in a solution of decreasing pH until the coating dissolved. Manganese began dissolving from the sand at a pH of less than 2.

Lui et al. (2001) published a study focusing on divalent heavy metal removal from storm water using manganese oxide coated polymeric media (MOPM). The report included an analysis of the characteristics of the MOPM. Figure 2-6 shows the results of an SEM analyses of uncoated and coated media. Figure 2-6 clearly shows the smooth surface of the uncoated media and the rough, porous nature of the manganese coating. The authors found that the MOPM had a much larger specific surface area than uncoated media at 27.34 m^2/g media, and a coating of 6.37 mg of Mn per g of media. Using EDS, the major elements of the coating were determined to be Mn and O. The SEM image also shows irregular pores in the oxide surface. The diameters of these pores were estimated to range from 0.1 μm to 5 μm. The authors conclude that these micro pores and macro pores facilitate intra-aggregate transport that must be taken into consideration with respect to the kinetics of adsorption of metal ions. The thickness of the coating was estimated to range from 20 μm to 200 μm.

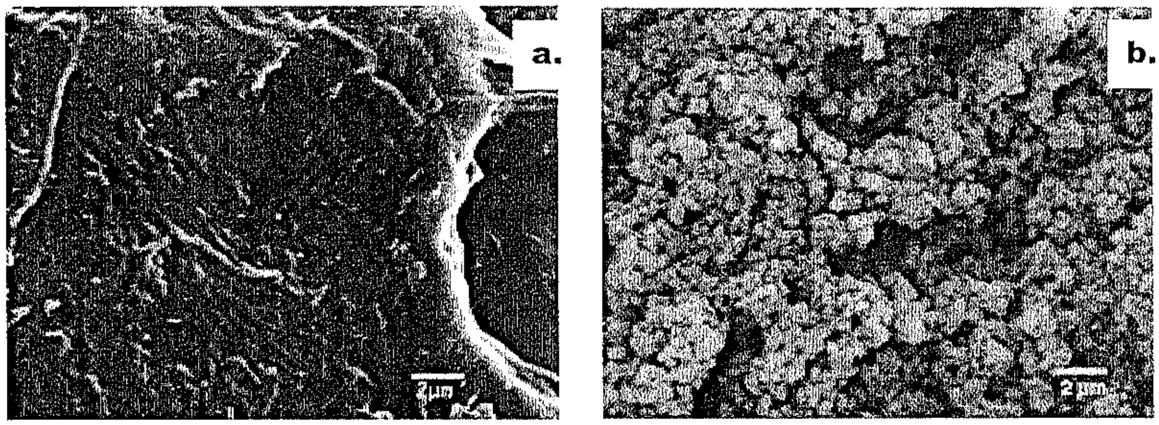

Figure 2-6 (a.) Uncoated Polymeric Media and (b.) Coated Polymeric Media (From Lui et al. (2001))

Lui et al (2001) also calculated the surface charge of the MOPM as a function of pH. These results are shown in Figure 2-7. In the pH range of 6 to 8, the MOPM possessed a negative surface charge which the authors state could be advantageous to the adsorption of positively charge metallic cations due to electrostatic interactions.

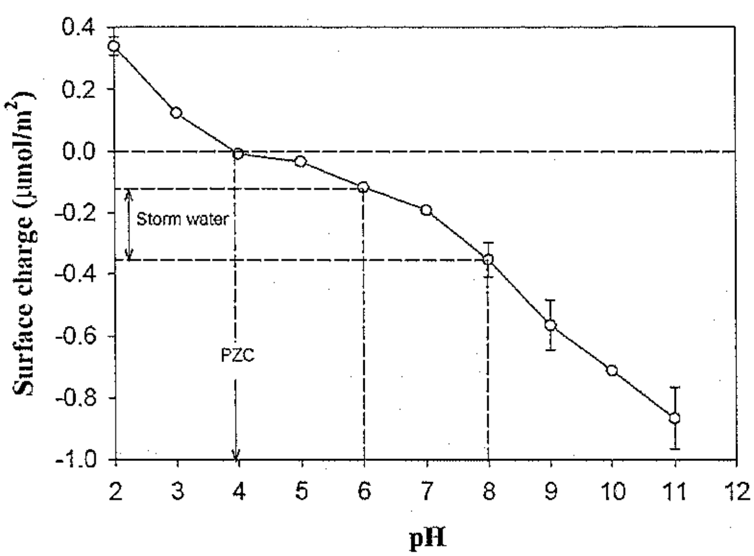

Figure 2-7 Net Surface Charge of MOPM as a function of pH (From Liu et al. ((2001))

3.0 Materials and Methods

This chapter contains a description of the methods and materials used in this study. Section 3.1 contains the general experimental design. The remaining sections present the detailed experimental and analytical methods, and the materials, used in the work. Table 3-1 summarizes basic information for the participating WTPs studied for this report.

Table 3-1 Summary of Participating WTPs

Plant	Capacity (MGD)	Clarification	Filter Media	Media Installation
Brown (Durham, NC)	30	Lamella Sedimentation	24 in Anthracite/12 in Sand	1981, 1991 and 2000
Harwood's Mill (Newport News, VA)	36	Lamella Sedimentation	30 in Anthracite/12 in Sand	1989
Sobrante (EBMUD, CA)	55	Lamella Sedimentation	30 in Anthracite/15 in Sand	2002
USL (EBMUD, CA)	55	Lamella Sedimentation	24 in Anthracite/15 in Sand	2002
Carno (Welsh Water, UK)	2.4	Dissolved Air Flotation	2 Stage: 39 in Sand per Stage	May 2005
Canteraf (Welsh Water, UK)	8.5	Dissolved Air Flotation	2 Stage: 29 in Sand per Stage	1995
Trap Falls (AWC, CT)	25	Lamella Sedimentation	24 in Athracite/12 in Sand	Jun 1996
Warner (AWC, CT)	50	Dissolved Air Flotation	24 in Athracite/12 in Sand	Jun 1997
Stamford (AWC, CT)	24	Lamella Sedimentation	2 Stage: 11 in Sand per Stage	1987

3.1 General Experimental Design

The focus of this study was the characterization of oxide coated filter media from nine participating water treatment plants (WTPs). Filter media was sampled from these plants using different methods. For one utility, the media filters were sampled after water was removed from the filters. At this point a sampling devise was driven through the filters and a dry core was taken. For another treatment plant only the top of the filter was accessible, so grab samples were taken. For the remaining utilities sampling was done when the filters were in high rate backwash. At this point, with the media fluidized, a sampling devise was inserted into the media and a wet core was taken.

After sampling, media samples were taken or sent to the UMass Environmental Engineering laboratory. At the laboratory the samples were analyzed for Mn uptake, metal oxide coating level, surface area, and size. Mn uptake was measured using a standard protocol developed for this study. The oxide coating level was measured by extracting the metal coating from the filter media using a strong reducing and acidic environment. The surface area of the media samples were measured by nitrogen (N_2) adsorption. The size of the media was measured using the ASTM standard sieve analysis for filter media.

An additional objective of this research was to evaluate manganese removal at the participating WTPs. Samples of raw water and filter effluent were taken from some of WTPs and analyzed for metals concentration at the UMass Environmental Engineering laboratory. Other plants participated in this aspect of this study by sending water quality data to UMass.

3.2 *Experimental Methods*

The following section provides in-depth information pertaining to the methods used for this study.

3.2.1 Media Sampling

The majority of the media sample cores were taken during a period of high rate filter backwash. Typically, two cores were taken for each filter. For sampling in this manner, a media coring device described in AWWA Opflow (Soucie, 2003) was adapted. The device consists of 2 in diameter clear schedule 40 polyvinyl chloride (PVC) pipe. Additional sections of 2 in PVC pipe with threaded couplings were used to provide additional depth for the device when required. A tennis ball was fastened to the end of a rope that was strung through the length of the PVP pipe. When the sampling device was lowered into the filter bed, the tennis ball could be pulled tight to seal the bottom of the pipe and allow a core of media to be lifted from the filter. The media sampling device was sent to utilities that did not have a similar sampling device.

Samples from the Carno and Cantref Water Treatment Works (WTWs,) in the United Kingdom (UK) were collected in a different manner. The filters were taken off-line and drained. Then, a coring device was driven through the dry filter media. After the coring device had reached the bottom of the filter bed, the bottom of the coring device was closed and a core of media was removed from the filter.

Once a media core was taken from a filter, the water was drained and the sample was extruded from the PVC pipe into roughly 6 inch long sub-samples. The media sub-samples were placed in jars and filled with filter effluent. Samples were then stored in a cooler during transport to UMass. At UMass samples were stored wet and placed in a 4 deg C, walk-in refrigerator. If samples needed to be stored wet for an extended period of time, the water in the media jar was changed to ensure aerobic conditions. Eventually, all samples were air dried at 30 deg C and low humidity for long term storage.

3.2.2 Media Extractions

To measure the amount of metal in the oxide coating on the surface of the media, the oxide coating was dissolved and then the concentrations of the various metals in solution were measured. The oxide coating was dissolved by placing the media in an acidic, reducing solution. The media was first rinsed with de-ionized (DI) water to remove materials that were not associated directly with the oxide coating. A small amount of the wet media was then dried in a 105 deg C oven. The amount of wet media dried was selected to yield approximately 1.0 gram of dry media. After drying for 24 hours, the media was removed and allowed to cool in a dessicator, then weighed.

After the mass of media was determined, the media sample was placed in 250 mL of a 1.0% nitric acid solution. Approximately 1 gram of hydroxylamine sulfate (HAS) was added to the solution. HAS is a reducing agent which was used to increase the rate of dissolution of the oxide coating. The solution was then covered, shaken, and allowed to react for at least 6 hours.

At the end of the 6 hour reaction time, the solution was filtered through a 0.7 μm Whatman fine, glass-fiber filter (GF/F). The concentrations of metals in the solution (Al, Fe, Mn and occasionally Ca and Cu) were analyzed using an inductively coupled plasma (ICP) atomic emission spectrophotometer (AES). Once the concentrations of the metals were measured, the amount of oxide coating was calculated using the following equation:

$$Metal\ Oxide\ Coating\ (mg\ metal\ /\ gram\ media) = \frac{([metal] * Vol)}{mass\ of\ media} \qquad \textbf{Equation 3-1}$$

where;

[metal] = metal concentration in extraction solution (mg/L)

Vol = volume of extraction solution (L)

mass of media = dry weight of media extracted (g)

3.2.3 Manganese Uptake Determination

3.2.3.1 Recirculating Experiments

Mn uptake was characterized using a standard protocol developed for this study. A schematic of the set-up is shown in Figure 3-1. Media collected from the filter was rinsed with DI water on a sieve prior to being placed in the column. This was done to remove any material that was not directly associated with the oxide coating. A depth of approximately 3 cm of wet media was added to the 1.5 cm diameter column, resulting in a mass of 2 to 7 grams of dry media. The Mn solution reservoir contained 2 to 8 L of Mn solution. The volume of solution was chosen based on the anticipated Mn uptake of the media. The water quality parameters for the Mn solution are listed in Table 3-2. The solution was recirculated through the media column at a hydraulic loading rate (HLR) of 10 gpm/ft^2. During the 4 hour period, sampling of the Mn solution occurred at 60, 120, 180, 210 and 240 minutes. The Mn concentration in the solution was measured using the HACH© low range manganese method. Samples of the initial and final concentrations in the reservoir were also analyzed using ICP-AES.

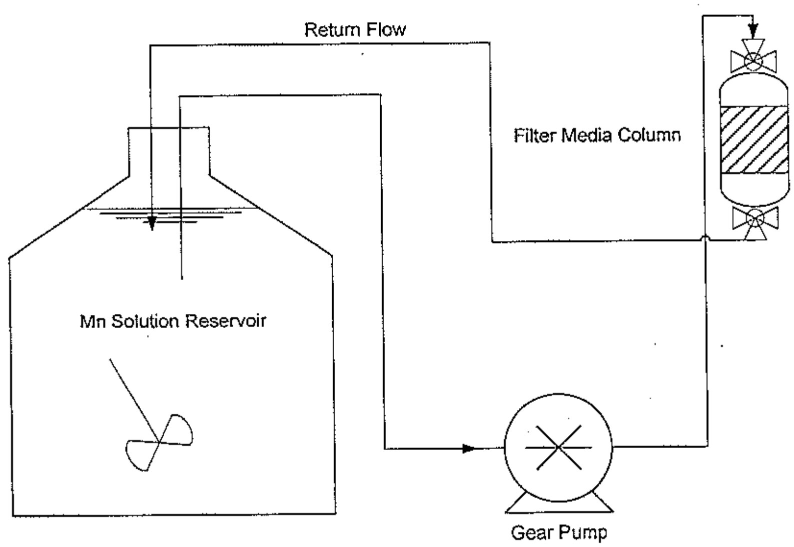

Figure 3-1 Mn Uptake Apparatus Schematic

Table 3-2 Water Quality Parameters of Mn Solution

Parameter	Value	Notes
Water	Laboratory DI	
pH	6.3 +/- 0.1	Adjusted with HCl and NaOH
Alkalinity	25 mg/L as $CaCO_3$	Added with $NaHCO_3$
Calcium	10 mg/L	Added with $NaCl_2$
Mn(II)	0.3 to 0.5 mg/L	Added as $MnSO_4$. Initial conc. of 0.5 mg/L. If conc. drops below 0.3 mg/L more $MnSO_4$ added

Following the initial Mn uptake experiment the now saturated media was rinsed with Mn free buffer solution. The media was then contacted with a re-circuiting solution of approximately 20 mg/L of HOCl for 12 hours to allow the adsorption sites on the oxide coating to regenerate. After the regeneration period, the media was again rinsed with a Mn free buffer solution. The Mn uptake experiment was then repeated to determine the regenerated Mn uptake. Following the second uptake experiment the media was removed from the column, dried in a 105 deg C oven and the dry weight was measured. The media uptake capacity was calculated by dividing the mass of Mn adsorbed by the dry weight of the media.

3.2.3.2 Once Through Experiments

Mn uptake experiments were also conducted using a flow through set up. This allowed an experiment to be run at the lab-scale that simulated conditions at the full-scale. This set up was used to determine the effect of pre-filter chlorination on sampled filter media. Figure 3-2 shows a diagram of a typical flow through experimental set up. This setup uses two pumps, one for a Mn solution and one for a chlorine (Cl_2) solution. The Cl_2 is dosed directly on top of the filter media in the column. Filter effluent samples were collected for analysis.

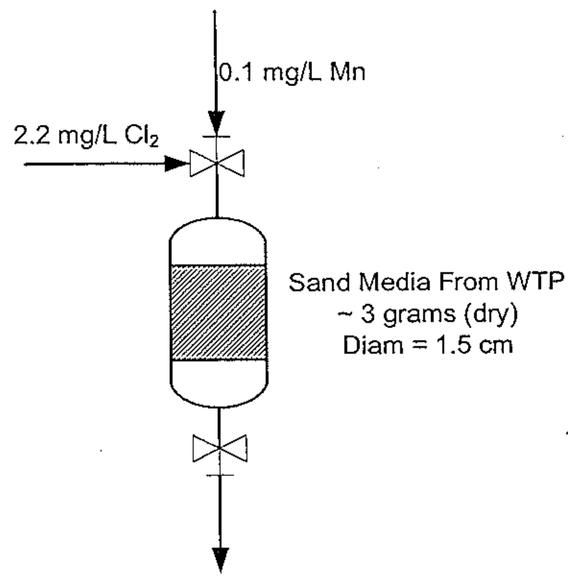

Figure 3-2 Schematic of Once Through Column Experiments

3.2.4 Full Scale Mn Removal Assessment

For several of the participating utilities, Mn concentrations were measured at selected points along the WTPs. Samples were sent/transported to UMass in coolers and stored in a 4 deg C refrigerator. The samples were acidified with HNO_3 to dissolve particulate metals and then filtered through a GF/F filter. The samples were then analyzed with an ICP mass spectrophotometer (MS) or ICP-AES. Details of both analytical methods are described in the following sections. When water samples were not collected directly from the participating utilities, water quality data from the utilities were sent to UMass.

Several sets of samples were collected for metal fractionation. Samples were collected directly at the treatment plant and filtered through a 0.4 μm membrane filter to differentiate between particulate and colloidal/dissolved metal. Subsamples were taken from the unfiltered and filtered water and analyzed using ICP-AES. The amount of metal in the unfiltered samples was recorded at total metal and the amount of metal in the filtered samples was taken as the dissolved metal. The amount of particulate metal was calculated as the difference of the two. For treatment plants that do not use strong oxidants, the colloidal fraction of Mn is typically very low, so a single filtration step is adequate.

3.3 *Analytical Methods*

3.3.1 Plastic and Glassware Preparation

Plastics and glassware were cleaned in a multi-stage process. First the glassware/plastics were washed with Alcanox© detergent and warm tap water. The containers were then placed in a sulfuric acid bath (10-20% H_2SO_4) for at least 24 hours. After removal from the bath the containers were rinsed thoroughly with DI water. Finally, non-volumetric glass containers were dried in a 190 deg C oven, while plastic and volumetric containers were dried in a warm (<50 deg C) convection drying oven.

3.3.2 Surface Area Measurement

A selection of samples were analyzed for surface area. The surface area of the oxide coated media was characterized by cryogenic N_2 adsorption using an automated instrument (Quantachrome AUTOSORB-1, Model No. ASIC-8). A five point Brunauer-Emmett-Teller (BET) method was used to evaluate the N_2 adsorption data and determine the surface area. Samples of dry media were out-gassed under vacuum for at least 8 hours at 85 deg C. After the analysis, the media was weighed on an analytical balance to determine its mass.

3.3.3 Sieve Analysis

Media size was measured using a sieve analysis. The sieve analysis was conducted as described in the ANSI/AWWA B100-01 standard for granular filter media (AWWA, 2001). Before sizing, media was dried in a low relative humidity (RH) constant temperature room. The temperature in the room was ~30 deg C with a humidity of 25%

RH. As per the standard, 100 grams of media was sieved through a set of eight sieves. The sieves used in each set were dictated by media type. Table 3-3 is a list of the sieve sizes used for each media type. The time of shaking for each media type was stipulated in the standard procedure. Anthracite media were shaken for 5 minutes and sand media were shaken for 10 minutes. After shaking, the media remaining on each sieve were weighed. The cumulative percent passing each sieve was plotted with a linear scale on the Y-axis and nominal opening size plotted on a log scale in the X-axis. From this plot the effective size (ES) of the media was estimated and the uniformity coefficient (UC) was calculated as shown in Equation 3-2 and Equation 3-3. If a media sample contained pieces of larger diameter under-drain gravel a number 10 sieve was added to the sieve set. Media retained on this sieve were not included in the results. Sometimes, after sieving, a substantial amount of black dust had collected in the pan of the sieve set. This material was also not included in the results of the sieve analysis as it was believed to be comprised of detached oxide coating.

$$ES = D_{10}$$ **Equation 3-2**

$$UC = \frac{D_{10}}{D_{60}}$$ **Equation 3-3**

where;

D_{10} = Size at which 10% (by mass) of sample passes (mm)

D_{60} = Size at which 60% (by mass) of sample passes (mm)

Table 3-3 Standard Sieve Sets for Each Media Type

Anthracite Media		Sand Media	
No. (US STD)	Size (mm)	No. (US STD)	Size (mm)
10	2.00	14	1.40
14	1.40	18	1.00
16	1.18	20	0.850
18	1.00	25	0.710
20	0.850	30	0.600
30	0.600	35	0.500
40	0.425	40	0.425
50	0.300	50	0.300

3.3.4 Soluble Metal Concentration Measurement

This section details the analytical methods used to measure the concentration of soluble metals. All methods were conducted using blanks and dilutions. Blank samples were DI water samples, acidified with HNO_3. Samples with a high expected metals concentration were diluted with DI water and then acidified to 1% HNO_3.

3.3.4.1 ICP-AES

The concentrations of metals (Mn, Fe, Al and Ca) were measured using three different ICP-AES instruments. All three instruments were located on the UMass campus; one in the Geosciences Department, one in the Environmental Institute laboratory and one in the Environmental Engineering laboratory. The majority of analyses were done using the ICP-AES located in the Environmental Engineering laboratory. The detection limit and calibration range for this instrument are listed in Table 3-4.

Table 3-4 Estimated Detection Limits and Maximum Calibration Range for ICP-AES

Metal	Estimated Detection Limit (mg/L)	Max. Calibration Range (mg/L)
Mn	0.003	20
Al	0.003	20
Fe	0.003	20
Ca	0.004	20

3.3.4.2 ICP-MS

Some water samples with low levels (<0.2 mg/L) of Mn were analyzed on an ICP-MS (ELAN DRC-e ICP-MS, PerkinElmer Corp, Wellesely, MA). The instrument was located in the UMass Environmental Engineering laboratory. The samples were acidified with HNO_3 then filtered using a GF/F filter. The ICP-MS was calibrated up to 0.2 mg/L of Mn. The estimated detection limit is comparable to the detection limit of the ICP-AES method.

3.3.4.3 HACH© Low Range Manganese Method

Manganese concentrations were measured using the HACH low range (0.005-0.7 mg/L) manganese test (Method 8149) during the uptake experiments. A volume of 10 mL of solution was placed into the sample cell using a pipette. A pre-measured ascorbic acid powder pillow, 15 drops of alkaline cyanide reagent, and 21 drops of PAN indicator were added. The contents of the cell were shaken and allowed to react for two minutes. The manganese concentration was then measured using a HACH DR/4000 spectrophotometer. The instrument contains HACH program 2260 which includes an internal calibration curve. The program measures the absorbance of the solution at a wavelength of 560 nm then converts that value to a Mn concentration. The program was zeroed using a DI water blank. The results from the HACH method were checked versus a set of ICP-AES results and were found to be within 10% of the ICP-AES results for concentrations above 0.02 mg/L. At concentrations less than 0.02 mg/L the HACH results were not within 10% of the ICP-AES results. The detection limit of the HACH method is stated by HACH as 0.005 mg/L.

3.3.5 pH Measurement

All pH readings were taken with a bench-top meter (Thermo Electron Corp. Model No. 720Aplus). An AccupHast (Thermo Electron Corp) variable temperature electrode was used with the meter. The system was calibrated regularly. Proprietary buffer solutions of pH 4, 7 and 10 were used in the calibration process.

3.3.6 Mass Determination

Media mass measurements were made using an Adventure Analytical Balance (Model No. AR-1140, Ohaus Corp. Pine Brook, NJ). The balance has an accuracy of 0.0001 grams. The weighing of HAS regent was done on a separate top loading balance (Model No. Galaxy 4000D, Ohaus Corp. Pine Brook, NJ). The balance had a accuracy of 0.01 grams.

4.0 Results and Discussion

This research is focused on nine surface water treatment plants. Historical raw and filtered Mn concentrations were obtained and each plant's filter media were sampled and characterized at the UMass Environmental Engineering laboratory. The media's metal coating levels, size, surface area and Mn uptake capability were determined. This chapter presents a discussion of the results of this characterization which is divided into two sections. In Section 4.1, the characteristics of each treatment plant studied are presented. The characteristics covered include overall treatment process, raw water quality, media size and metal oxide coating levels. Section 4.2 contains an analysis of the metal oxide coating results. The statistical variability and temporal variability are quantified. The effect of raw water and treatment conditions on the metal oxide ratios are discussed as well as the effect of coating on surface area and Mn adsorption capability.

Several sampling events were conducted at each participating WTP. However, only selected results from certain sampling events are discussed in this report. Table 4-1 shows each sampling event conducted during this entire study. Results from AWC plants not discussed here can be found in the work of Bouchard (2005). Results for most metal extractions are found in Appendix A.

Table 4-1 Summary of Sampling Events

Utility Name	Sample Date	No. of Cores	Collection Method	Type of Media
Appomatox	5/19/2005	6	Coring Device	GAC/Sand
AWC - Easton	1/12/2005	2	Coring Device	Anthracite/Sand
AWC - Easton	3/3/2005	1	Coring Device	Anthracite/Sand
AWC - Easton	5/24/2005	2	Coring Device	Anthracite/Sand
AWC - Stamford	1/12/2005	samples only	Grab Sample	2 Stage Sand
AWC - Stamford	3/3/2005	samples only	Grab Sample	2 Stage Sand
AWC - Stamford	5/24/2005	samples only	Grab Sample	2 Stage Sand
AWC - Stamford	8/15/2005	samples only	Grab Sample	2 Stage Sand
AWC - Trap Falls	1/11/2005	4	Coring Device	Anthracite/Sand
AWC - Trap Falls	8/16/2005	6	Coring Device	Anthracite/Sand
AWC - Warner	1/11/2005	5	Coring Device	Anthracite/Sand
AWC - Warner	4/5/2005	4	Coring Device	Anthracite/Sand
AWC - Warner	8/17/2005	4	Coring Device	Anthracite/Sand
AWC - Warner	01/10/06	2	Coring Device	Anthracite/Sand
Durham	6/1/2005	7	Coring Device	Anthracite/Sand
Durham	11/29/05	6	Coring Device	Anthracite/Sand
EBMUD - Sobrante	6/29/2005	2	Coring Device	Anthracite/Sand
EBMUD - Sobrante	12/13/05	2	Coring Device	Anthracite/Sand
EBMUD - USL	6/17/2005	2	Coring Device	Anthracite/Sand
Newport News	5/2/2005	2	Coring Device	Anthracite/Sand
Newport News	10/31/2005	2	Coring Device	Anthracite/Sand
Newport News	5/7/2006	2	Coring Device	Anthracite/Sand
Passiac Valley	10/20/2005	2	Coring Device	GAC/Sand
UK - Cantref	9/12/2005	2 per stage	Dried Core	2 Stage Sand
UK - Carno	9/12/2005	2 per stage	Dried Core	2 Stage Sand

4.1 Treatment Plant Characteristics

This section contains a discussion of the treatment plant characteristics. Each participating WTP is presented individually. The focus is on the overall treatment process, raw water quality, the size of the filter media and the metal coating levels.

4.1.1 Trap Falls Water Treatment Plant – AWC

4.1.1.1 Treatment Process

The Trap Falls WTP (Aquarion Water Company) treats influent from the Trap Falls Reservoir. The plant has a capacity of 25 MGD. The treatment process includes alum coagulation, flocculation, plate sedimentation, dual media (anthracite over sand) filtration and disinfection. The Trap Falls WTP uses alum for coagulation. The target coagulation pH range in the summer months is 6.5 to 6.8 and 6.6 to 6.9 in the winter. Filtration is conducted via six oxide coated, dual media filters. The media were installed in 1996. The average effective size (D_{10}) of the anthracite in the filters was 0.83 mm. The D_{10} of the sand layers of the filters was 0.49 mm. During the installation process, filters numbered 1 through 4 were pre-coated with Mn oxide by a processes involving $KMnO_4$. Filters 5 and 6 were not pre-coated.

Chlorine is used for oxide coating regeneration and disinfection. The chlorine is dosed at two locations, between sedimentation and the filters, and at the entrance to the clearwell. The pre-filter dose is determined based on a filter effluent concentration goal of 0.8 mg/L of Cl_2. The Cl_2 dose prior to the clearwell is approximately 1.2 mg/L. This dose was chosen based on disinfection requirements and for distribution system chlorine residuals goals. Between January and June 2005, the pre-filter chlorine dose was decreased such that the filter effluent chlorine residual was 0.2 mg/L.

4.1.1.2 Raw Water Quality

Figure 4-1 shows historical raw water Mn concentrations at Trap Falls, taken monthly for 1998 to 2004 and weekly from January 2005 to January 2006. The plot shows relatively low manganese concentrations, less then 0.1 mg/L, for the majority of the year. During the late summer months there was typically an increase in manganese concentration to 0.6 mg/L, corresponding to the period of lake stratification and turn-over. For the 2005 calendar year, the average Mn concentration was 0.04 mg/L with a maximum Mn concentration of 0.22 mg/L.

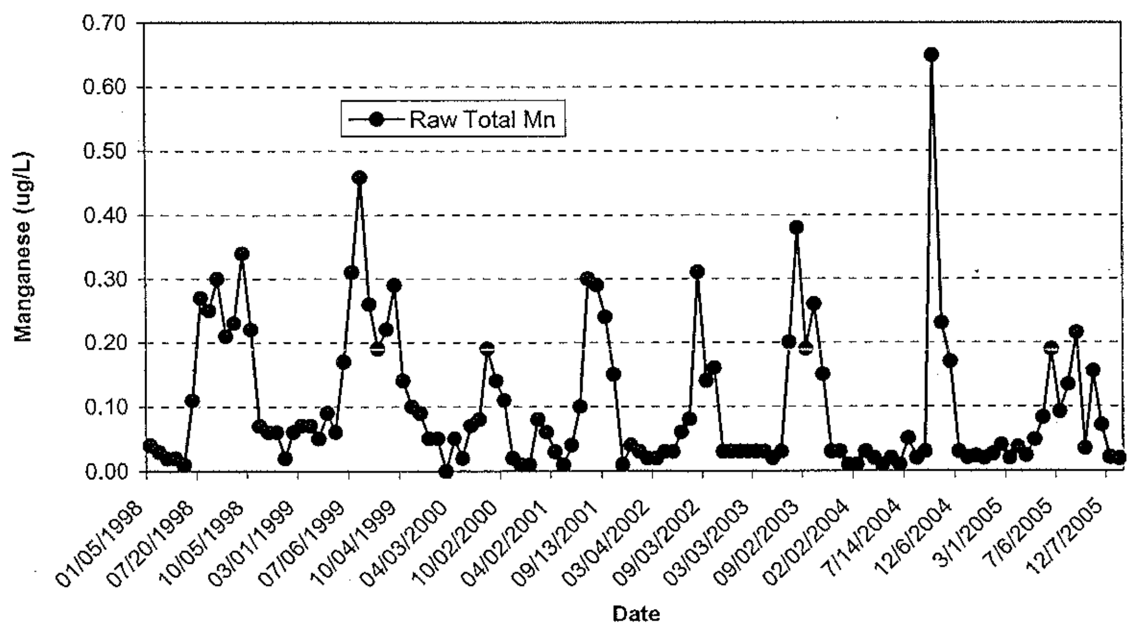

Figure 4-1 Trap Falls Raw Water Mn Concentration for 2005

4.1.1.3 Metal Coating Level

One media sampling at the Trap Falls WTP was conducted on August 16, 2005. Six cores were taken from filter 6, which was not pre-coated with Mn when installed. All cores were taken during high rate filter backwash. The media samples were extracted and metal concentrations were measured. Figure 4-2 shows profiles of manganese, aluminum and iron coating levels versus filter depth for two for the filter cores. The results show a typical profile, with the top anthracite layers having more coating than the bottom sand layers. This is probably due to significant metal uptake in the anthracite layer such that the lower sand media is not exposed to high levels of dissolved Mn. Figure 4-2 shows that the top anthracite layers had Mn oxide coating levels of 36-40 mg of Mn per gram of media. The amount of Mn oxide coating in the sand layers was much less, at 0.28-0.68 mg of Mn per gram of media. The middle depth core often contains a mixture of anthracite and sand, so the net coating level reflects this mixture.

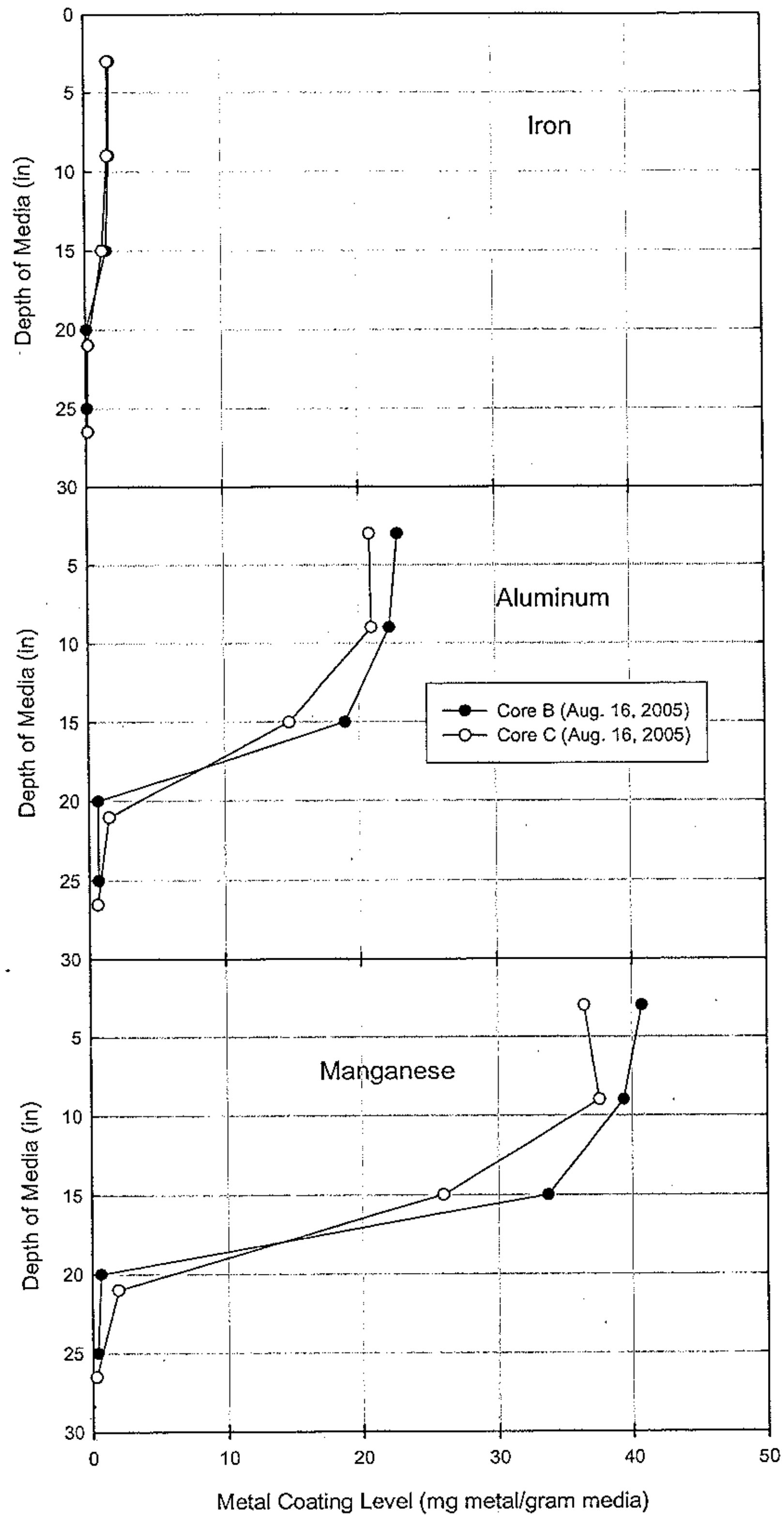

Figure 4-2 Trap Falls Media Metal Coating Levels

The depth profiles for the Al and Fe coating levels are similar to the Mn profile, although the metals concentrations in general are less. The top anthracite layers had 20-22 mg Al per gram of media while the bottom sand layers had 0.62-0.71 mg Al per gram of media. The elevated levels of aluminum coating might be caused by the use of alum as a coagulant. Soluble aluminum may adsorb to the media in a similar fashion to Mn. Also particulate Al may be deposited on the media by particle filtration.

The Fe coating in the anthracite layers ranged from 1.6-1.9 mg Fe per gram of media, while the sand layers had 0.10-0.21 mg of Fe per gram of media. In general, there is much less Fe coating on the filter media than Mn coating. However, the concentrations of Fe and Mn in the raw water are similar. The lower Fe level can be attributed to the ease by which Fe is oxidized compared to Mn. In the presence of HOCl, a significant amount of Fe will be oxidized prior to adsorption on the filter media, so is removed as particles which are detached from the media by backwashing. Also, a significant fraction of the raw water Fe may be particulate and may be removed during settling of DAF.

4.1.2 Warner WTP – AWC

4.1.2.1 Treatment Process

The Warner WTP (Aquarion Water Company) treats influent from the Hemlocks Reservoir. The plant has a capacity of 50 MGD. The treatment process includes coagulation, flocculation, dissolved air flotation (DAF) over dual media filtration and disinfection. The raw water at Warner WTP is coagulated with a combination of alum and cationic polymer. The pH range for coagulation is 6.3-6.5 in the summer and 6.7-6.9 in the winter. Flotation and filtration are conducted via nine parallel trains each oxide coated dual media filters. The filter media was installed in June of 1997. At the time of installation, the media were pre-coated with manganese oxide using a process with potassium permanganate. The average D_{10} of the anthracite and sand in the filters were 0.80 mm and 0.50 mm respectively.

Chlorine is used at Warner WTP for disinfection as well as oxide coating regeneration. DAF clarification occurs directly above the dual media filters, meaning that the separation zone of the DAF tank sits directly above the filter bed. For pre-filter chlorination, chlorine is dosed as water flows from the contact zone to the separation zone. Chlorine is dosed to establish a filter effluent residual of 0.7 to 0.9 mg/L of chlorine. Chlorine is also dosed as the water enters the clearwell in order to maintain a residual of ~1 mg/L entering the distribution system.

In January 2005, pre-filter chlorination was discontinued for four of the nine treatment trains. Filters 8 and 9 received no chlorine in all of 2005 while chlorination was resumed on filters 1 and 2 in the summer of 2005. AWC made changes to potentially decrease chlorine use and the formation of disinfection by-products.

4.1.2.2 Raw Water Quality

Figure 4-3 shows historical raw water Mn concentrations at the Warner WTP. The samples were collected monthy from 1998-2004 and bi-weekly from January 11, 2005 to

December 28, 2005. The plot shows relatively low manganese concentrations (<0.05 mg/L) for the majority of the year. During the fall season there was typically an increase in manganese concentration to 0.2 mg/L, possibly corresponding to turn over after a period of lake stratification. For the 2005 calendar year, the average Mn concentration was 0.02 mg/L with a maximum Mn concentration of 0.105 mg/L.

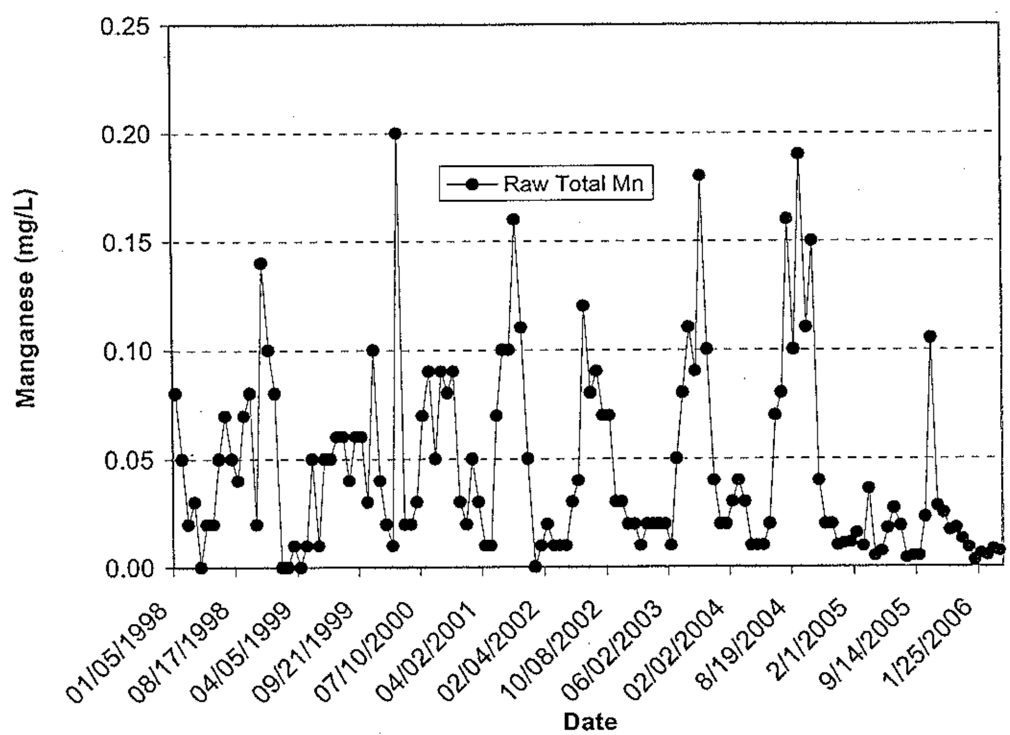

Figure 4-3 Warner Raw Water Mn Concentration

4.1.2.3 Metal Coating Levels

Two of the media sampling at the Warner WTP was performed on August 17, 2005 and January 10, 2006. Two cores each were taken from filters 7 and 9. During the course of this study, filter 7 was continuously pre-chlorinated, while filter 9 was not. The filters sampled were chosen to enable an evaluation of possible effects of cessation of pre-filter chlorination. All media samples were extracted and metal concentrations were determined. Both sampling events in Figure 4-4 show profiles of Mn, Al and Fe coating levels versus filter depth. The depth profiles for the metal coatings are similar to those for the Trap Falls dual media. The top anthracite layers had Mn coating levels of 8.2-14 mg Mn per gram media while the lower sand layers had Mn coating levels of 0.13-2.5 mg Mn per gram of media. There was a general increase in Mn coating in the cores between the two sampling dates. Further discussion of the Mn coating variability occurs in Section 4.2.

The depth profile for the Al and Fe coating levels is similar to the Mn profile. In the Warner WTP the levels of Al were almost identical to the Mn concentrations. Al coating levels in the anthracite layer ranged from 8.5-14 mg Mn per gram of media. The sand layers had Al levels between 1.0-3.2 mg Al per gram of media. Alum is used as a coagulant at Warner WTP which could attribute to the observed Al coating levels.

The Fe coating in the anthracite layers ranged from 0.34-1.9 mg Fe per gram of media and 0.02 to 0.21 mg Fe per gram of media in the sand layers. The Fe coating levels are consistently much lower than the Mn coating levels, but follow a similar profile.

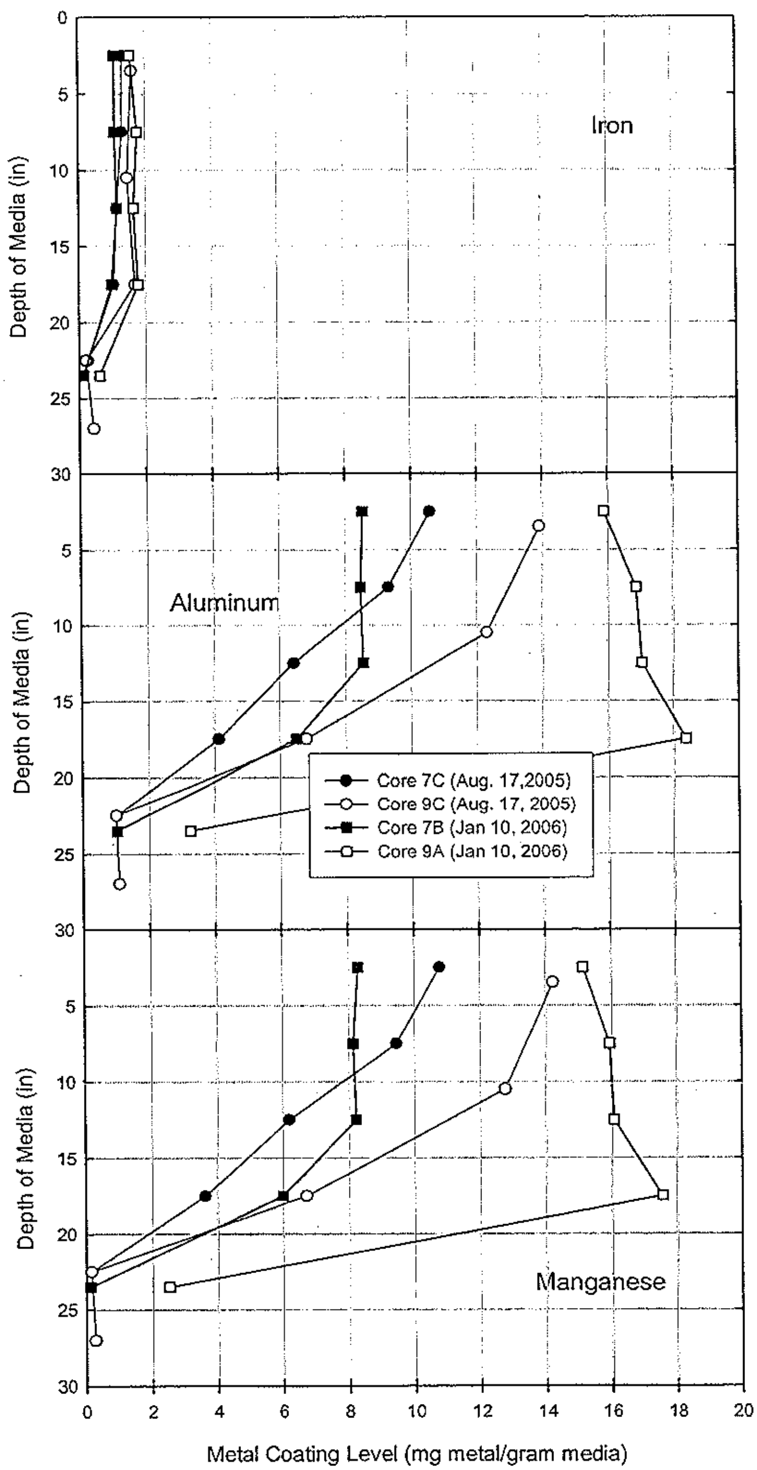

Figure 4-4 Warner Media Metal Coating Levels

4.1.3 Stamford WTP - AWC

4.1.3.1 Treatment Process

The Stamford WTP (Aquarion Water Company) treats influent from the Laurel and North Stamford Reservoirs. The plant has a capacity of 24 MGD. The treatment process includes coagulation, flocculation, conventional sedimentation, two-stage sand filtration and disinfection. The raw water at Stamford WTP is coagulated with alum. The target pH range for coagulation is 6.3-6.5 in the summer and 6.7-6.9 in the winter. Filtration is conducted with four, parallel, two stage filters. The majority of Mn removal occurs in the first filter stage, as pre-filter chlorination occurs directly before this stage. There is no additional chlorination between the first and second stage of the filters. Sand media is used in both stages of filtration. The sand media in the first stage filters was installed in 1987. The sand media in the second stage filters was installed in 1999. Previously, the second stage filters had granular activated carbon (GAC) media. The average D_{10} of the sand in the filters was found to be 0.70 mm. The media depth is only 11-12 inches in the automatic backwashing filter.

The filter media at Stamford WTP is backwashed using a traveling bridge with backwashing of short individual filter sections with no access to the media. Therefore, complete cores of filter media could not be taken. Rather, samples from the top several inches of the filter media were taken.

Chlorine is used at Stamford WTP for disinfection as well as oxide coating regeneration. Chlorine is dosed to the water immediately following sedimentation. The pre-filter dose is set in order to achieve a filter effluent chlorine residual goal of 0.7 to 0.9 mg/L from the first filtration stage. Chlorine is also dosed to the clearwell to meet disinfection and distribution system residual requirements. The chlorine dose to the clearwell is determined based on a residual goal of 1.3 mg/L.

4.1.3.2 Raw Water Quality

Figure 4-5 shows historical raw water Mn concentrations at the Stamford WTP. The samples were collected bi-weekly from January 11, 2005 to November 2, 2005. The plot shows relatively low manganese concentrations for the majority of the year. During the late summer months there was an increase in manganese concentration to over 0.6 mg/L, corresponding to the period of lake stratification. For the period of sampling, the average Mn concentration was 0.03 mg/L with a maximum Mn concentration of 0.64 mg/L.

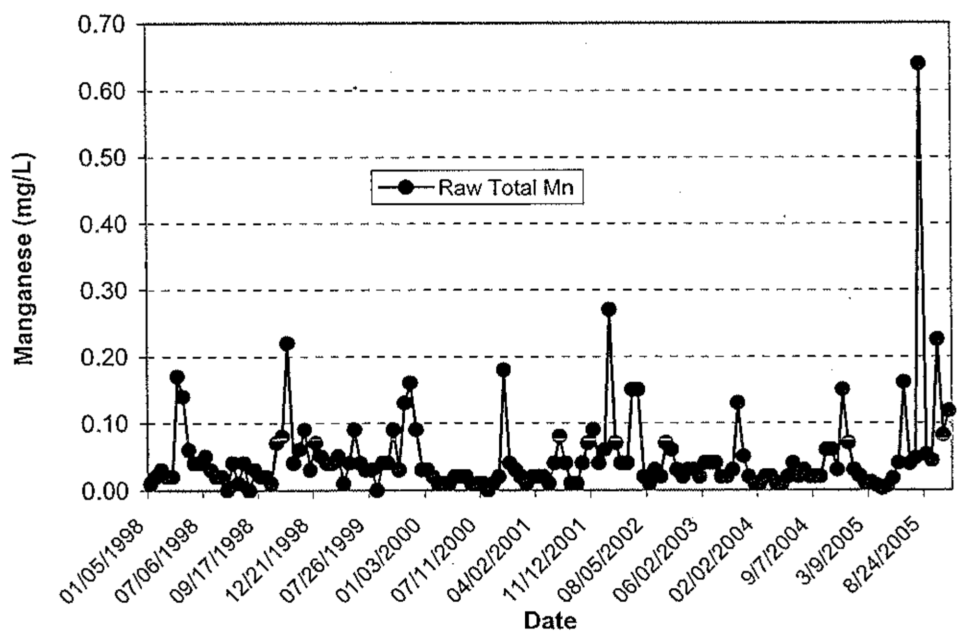

Figure 4-5 Stamford Raw Water Mn Concentrations

4.1.3.3 Metal Oxide Coating Levels

Media sampling was conducted at the Stamford WTP on August 23, 2005. Four sub-samples were analyzed for metal coating levels for each sample. The results from the August 23, 2005 sampling event are shown in Table 4-2.

Table 4-2 Stamford Media Oxide Coatings

Metal Coating Levels (mg metal per gram media)				
Sample Name	Filtration Stage	Mn	Al	Fe
S-1	1	25.4	27.4	2.42
S-2	1	28.8	31.4	2.82
S-3	1	29.9	30.6	2.70
S-4	1	31.0	31.1	2.74
S-5	2	0.001	0.038	0.004
S-6	2	0.001	0.081	0.004
S-7	2	0.001	0.043	0.003
S-8	2	0.001	0.039	0.003

The average Mn, Al and Fe oxide coating levels for the stage one filters were 28.8, 30.1 and 2.67 mg metal per gram of media, respectively. The Al levels are very similar to the Mn levels, while the Fe coating levels were much less. The average Mn, Al and Fe oxide coating levels for the stage two filters were 0.001, 0.050 and 0.003 mg metal per gram of media, respectively. The higher level of Al in relation to Mn in this stage might be attributed to the deposition of particulate Al on the filter media. The second stage filters had much lower values for all measured metals. This is attributed to the removal of metals in the first stage and the younger age of the filter media (1999 vs. 1987 for stage 1).

4.1.4 Canteraf WTW – Welsh Water (UK)

4.1.4.1 Treatment Process

The Canteraf WTW treats surface water from the Canteraf Reservoir in Wales in the United Kingdom. The plant has a capacity of 8.5 MGD. The treatment process includes coagulation, flocculation, DAF clarification, two stage sand filtration and disinfection. The raw water at Canteraf WTW is coagulated with ferric sulfate. The average coagulant dose is approximately 26 mg/L. The target pH for coagulation for all months of the year is 5.5. Filtration occurs via four, parallel, two stage filters. The filter media in both stages was installed in 1995. The average D_{10} for the first and second stage media are 0.57 and 0.60 mm, respectively. Chlorine is added between the two stages, with no chlorine entering the first stage. pH adjustment to 8.4 with lime also occurs between the two stages. The combination of chlorine and increased pH provides optimum conditions for soluble Mn removal by the second stage filters

Chlorine is used at Canteraf WTW for disinfection was well as oxide coating regeneration. Chlorine is dosed at 0.55 mg/L to the water immediately before the second stage of filtration. Chlorine is also dosed prior to the clearwell to meet disinfection and distribution requirements.

4.1.4.2 Raw Water Quality

Figure 4-6 shows historical raw water Mn and Fe concentrations at the Canteraf WTW. The samples were taken once per month from January 2000 to November 2000. The plot shows relatively low manganese concentrations for the majority of the year, less than 0.1

mg/L. During the late summer months there was an increase in manganese concentration to over 0.15 mg/L to over 0.2 mg/L of Fe. For the time span of sampling, the average Mn and Fe concentrations were 0.068 and 0.088 mg/L, respectively. The maximum Mn and Fe concentrations were 0.164 mg/L and 0.207 mg/L, respectively. The average raw water pH during the sample period was 7.24. Also, the average turbidity was 2.14 NTU.

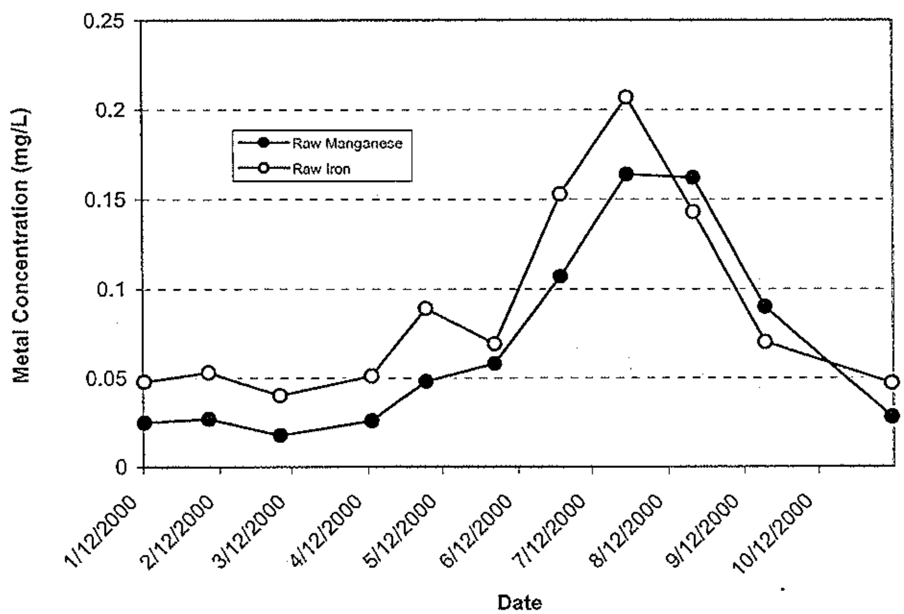

Figure 4-6 Canteraf WTW Raw Water Manganese and Iron Concentrations (2000)

4.1.4.3 Metal Oxide Coating Levels

Media sampling was conducted at the Canteraf WTW on September 8, 2005. The results for two cores each for the stage 1 and stage 2 filters are shown in Figure 4-7 and Figure 4-8, respectively, which show metal coating levels as a function of depth.

For stage one, the average Mn, Fe, Al and Ca concentrations were 0.09, 22.65, 0.99 and 0.41 mg metal per gram of media, respectively. For stage two, the average Mn, Fe, Al and Ca concentrations were 73.9, 44.9, 7.47 and 16.1 mg metal per gram of media. The relatively high values for Mn in the stage two filters show the effects of the lime and chlorine addition between the two stages. The elevated amounts of calcium on the stage 2 filter media might be attributed to the use of lime as a pH adjustment between filter stages. The high iron levels in stage 1 and stage 2 are possible caused by the use of a ferric coagulant. Mn may be present in the ferric coagulant possibly as a contaminant, which may cause high Mn oxide coating levels despite only moderate Mn concentrations in the raw water.

Figure 4-7 and Figure 4-8 do not in general show a variable profile of metal concentration with filter depth as seen in the AWC dual media filter results. This is because the Canteraf WTW has a single type or homogenous filter media. During periods of backwash, the media completely mixes and randomly sorts itself in the filter following backwash. A few of the core B results do show significant depth variability.

Figure 4-8 shows a similar pattern in the depth profiles for each metal in the second stage filter, suggesting consistency in the ratio of the metals that in the media coating. Further discussion of metal ratios occurs in Section 4.2.

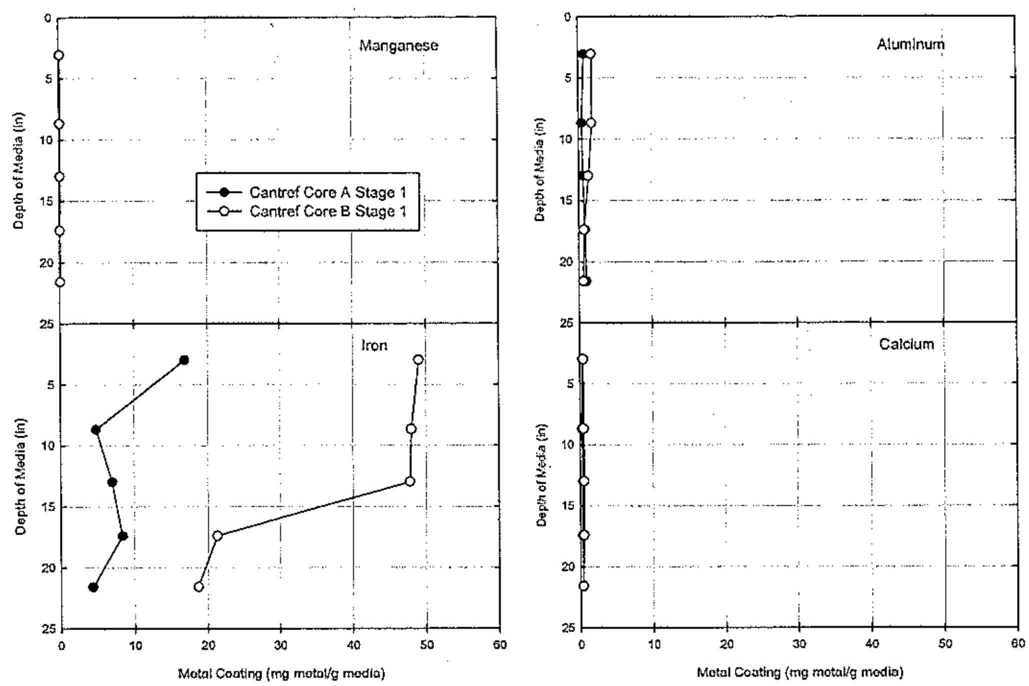

Figure 4-7 Canteraf Metal Coating Levels (Stage 1)

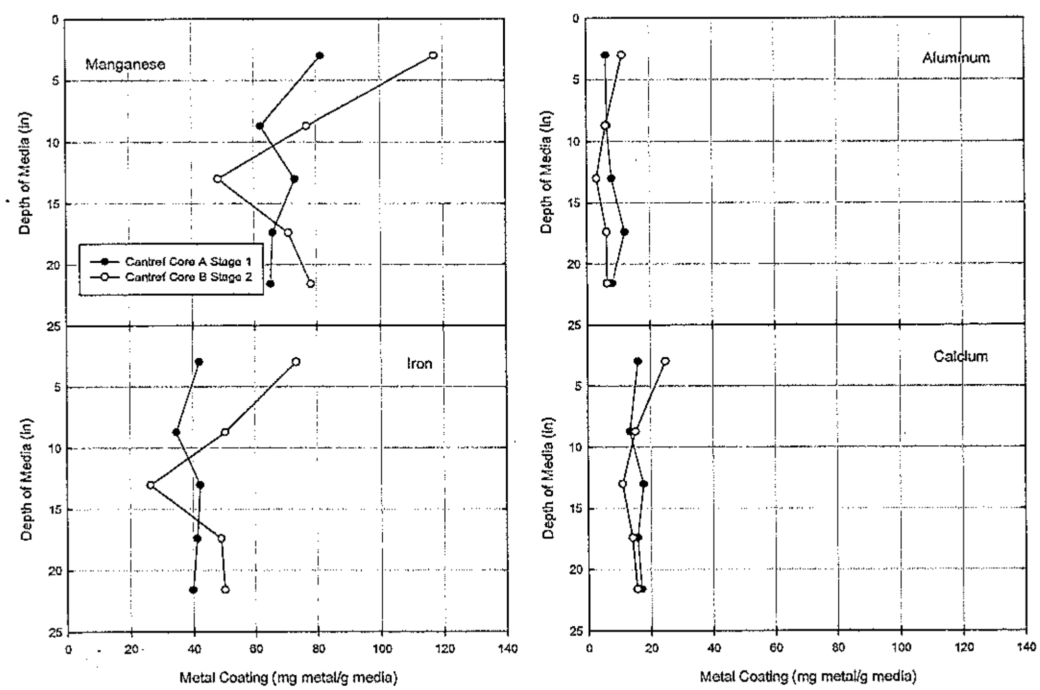

Figure 4-8 Canteraf Metal Coating Levels (Stage 2)

4.1.5 Carno WTW – Welsh Water (UK)

4.1.5.1 Treatment Process

The Carno WTW treats surface water from the Lower Carno and Upper Carno Reservoirs in Wales in the United Kingdom. The Lower Carno reservoir is normally used exclusively. The treatment process is similar to the process used at Canteraf WTW and includes coagulation, flocculation, DAF clarification, two stage sand filtration and disinfection. The raw water at Carno WTW is coagulated with alum. The coagulant dose is ranges from 80-140 mg/L as aluminum sulfate. The target pH for coagulation for all months of the year is 5.5. Filtration is conducted with parallel, two stage filters. The first stage has four filters and the second stage has three. The sand filter media in both stages were installed in 1999. The D_{10}'s for the first and second stage filters were 0.58 mm and 0.60 mm, respectively. The majority of Mn removal occurs in the second stage of filtration as pre-filter chlorination and pH adjustment occurs directly before the second stage.

Chlorine is used at Carno WTW for disinfection as well as oxide coating regeneration. Chlorine is dosed to the water immediately before the second stage of filtration. The pre-filter dose is 0.6 mg/L. Chlorine is also dosed prior to the clearwell to meet disinfection and distribution requirements.

4.1.5.2 Raw Water Quality

Figure 4-9 shows historical raw water Mn and Fe concentrations at the Carno WTW. The samples were taken several times per month from January 10, 2000 to August 15, 2005.

The results show periodically high levels of manganese (>1.5 mg/L). The average Mn and Fe concentrations for the time period provided were 0.24 mg/L and 0.36 mg/L respectively. The maximum concentrations for Mn and Fe were 3.76 mg/L and 1.03 mg/L respectively. The concentrations of both metals follow similar seasonal variation, with local maximums during the late summer. The raw water source had an average pH of 7.6 and an average hardness of 61.3 mg/L. The average turbidity of the raw water was 0.198 NTU. The average color of the raw water was 27.4 cu.

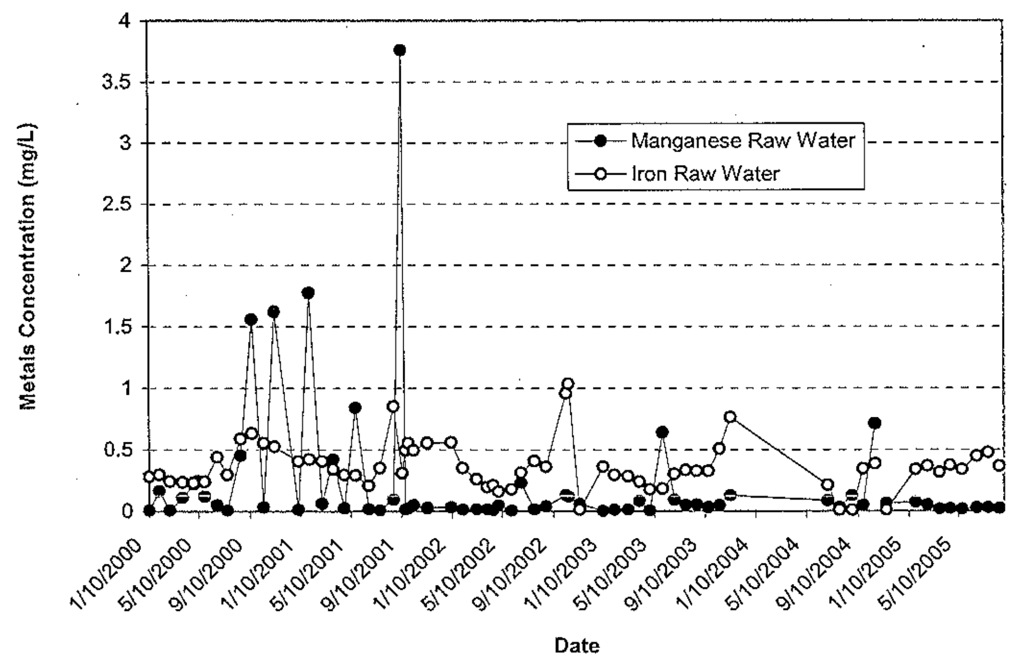

Figure 4-9 Carno WTW Raw Water Mn and Fe Concentrations for 2000-2005

4.1.5.3 Metal Coating Levels

Media sampling was conducted at the Carno WTW on September 7, 2005. The results for two cores for each filter stage are shown in Figure 4-10 and Figure 4-11 respectively.

For stage 1 the average Mn, Fe, Al and Ca concentrations were 0.14, 2.22, 2.46 and 0.64 mg metal per gram of media, respectively. For stage 2 the average Mn, Fe Al and Ca concentrations were 120, 9.26, 66.0 and 39.9 mg metal per gram of media respectively. The Mn oxide coating levels in stage 2 are the highest of any plant studied in this project, consistent with the high raw water Mn. Again, as for Canteraf, the low Mn coating in the first stage and the high level in the second stage show that application of free chlorine and the elevation in pH case Mn removal by the oxide coated media process. The elevated amounts of calcium on the stage 2 filter media might be attributed to the use of lime for pH adjustment between the filter stages. The elevated Al concentration and lower iron levels are probably related to the use of alum for coagulation, compared with ferric sulfate at Canteraf.

Figure 4-10 and Figure 4-11 do not show much variation in metal concentration with depth. As for the Canteraf WTW, the Carno WTW has homogenous sand filter media which mixes completely after backwash.

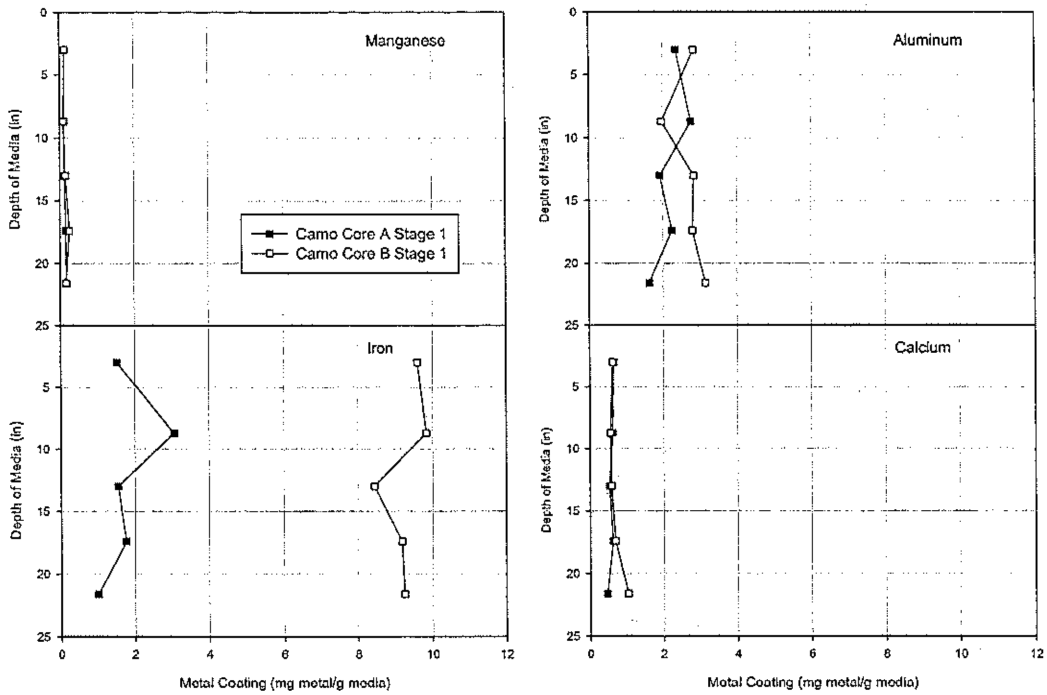

Figure 4-10 Carno Metal Oxide Coating Levels (Stage 1)

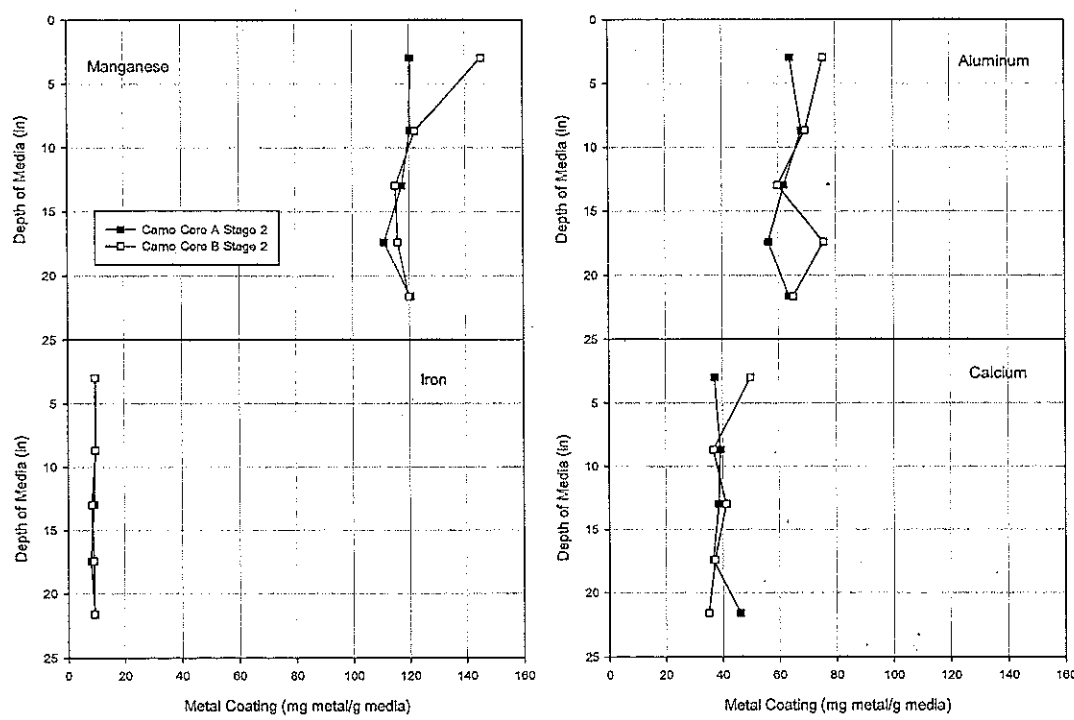

Figure 4-11 Carno Metal Oxide Coating Levels (Stage 2)

4.1.6 Wade G. Brown WTP – Durham, NC

4.1.6.1 Treatment Process

The William G. Brown WTP located in Durham, North Carolina, treats surface water from a terminal reservoir. The treatment plant has a capacity of 30 MGD. The treatment process includes coagulation, flocculation, sedimentation and dual media filtration. $KMnO_4$ may be used as a pre-oxidant in periods of high raw water Mn. The raw water at the Brown WTP is coagulated with ferric chloride. The pH range typically used for coagulation is between 5.8 and 6.3. Filtration occurs in seven parallel filters. The media in the filters were pre-coated with $KMnO_4$ prior to installation. The installation date for the filters varied. For the filters sampled in this study, Filter 4 was installed in the early 1980s, Filter 5 was installed in the early 1990s and Filter 7 was installed in 2003. The D_{10}s of the anthracite in filters 4, 5 and 7 are 0.40, 0.74 and 0.80 mm, respectively. Similarly, the D_{10}s of their respective sand layers are 0.34, 0.51 and 0.53 mm. The relatively smaller size of the oldest media, filter 4, may be due to the physical wear on the media during the years of operation.

Chlorine is used at the Brown TWP for disinfection and regeneration of oxide coated media. Chlorine is dosed to the water before and after filtration. Typical chlorine concentrations in the filter effluent range from 3-3.5 mg/L.

4.1.6.2 Raw Water Quality

The source water at the Brown WTP contains a significant amount of Mn and Fe. The pH ranges from 6.7-7.0. The raw water has moderate levels of TOC, and hardness and alkalinity values of approximately 30 mg/L as $CaCO_3$. The average pH was 6.7.

Figure 4-12 shows historical raw water Mn and Fe concentrations at the Brown WTP. Daily values were received, and then converted to monthly averages from January 2000 to July 2005. The average Mn and Fe concentrations for all months during this period were 0.23 and 0.59 mg/L respectively. The Fe concentration in the raw water was consistently higher than the Mn concentration. Concentrations of both metals varied seasonally although not always in a typical pattern seen with reservoirs. The maximum monthly concentration for Mn was 0.88 mg/L while the maximum monthly concentration for Fe was 2.04 mg/L.

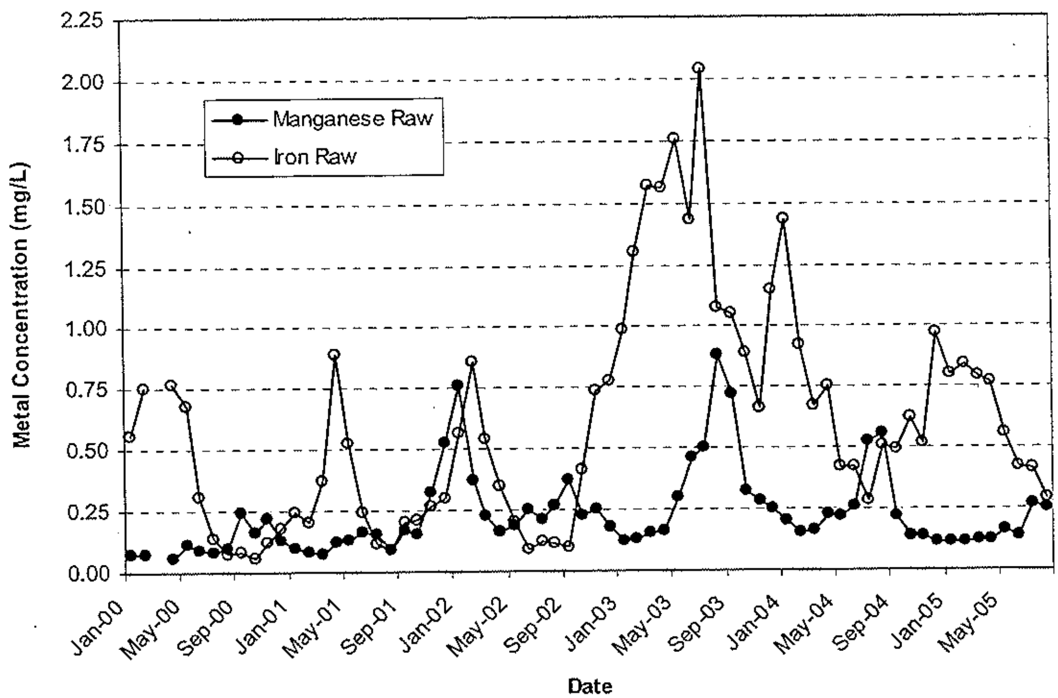

Figure 4-12 Brown WTP Total Raw Mn and Fe Concentrations 2000-2005

Figure 4-13 is a plot of daily raw water, total Mn and Fe concentrations at the Brown WTP for the 2004 calendar year. The plot of the daily data better illustrates the variation of the concentrations of both metals. In 2004, a typical pattern of a late summer maximum in Mn can be seen. There is also a local maximum in Fe concentration in the late summer, however the absolute maximum concentrations did not occur during that time. The maximum Mn and Fe concentrations for the year were 1.09 mg/L and 6.24 mg/L respectively. Also, the average Mn and Fe concentrations for the year were 0.25 mg/L and 0.66 mg/L respectively.

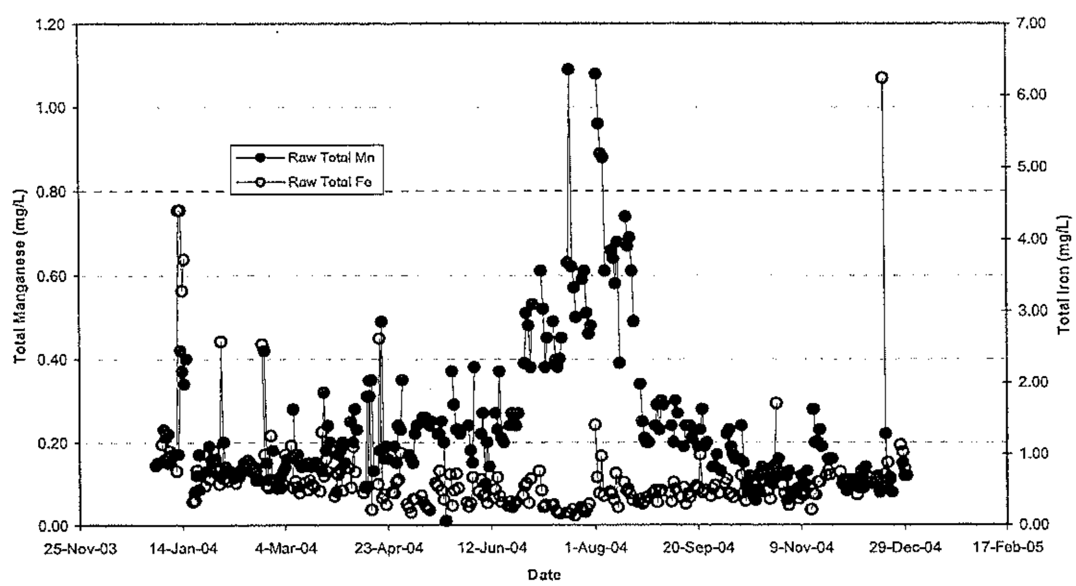

Figure 4-13 Brown WTP Daily Total Raw and Fe Concentrations 2004

4.1.6.3 Metal Coating Levels

Sampling at the Brown WTP occurred on two occasions, June 1, 2005 and November 29, 2005. Two cores were taken from three different filters, numbers 4, 5 and 7. During the November 2005 sampling event filter 4 was not available for sampling so two cores were taken from filter 3 as a substitute.

The three filters sampled, in both events, were chosen because they had been in service for different amounts of time. The metal coating profiles for the June and November sampling events are shown in Figure 4-14 and Figure 4-15, respectively. In each figure, the year of media installation is shown in the figure legends.

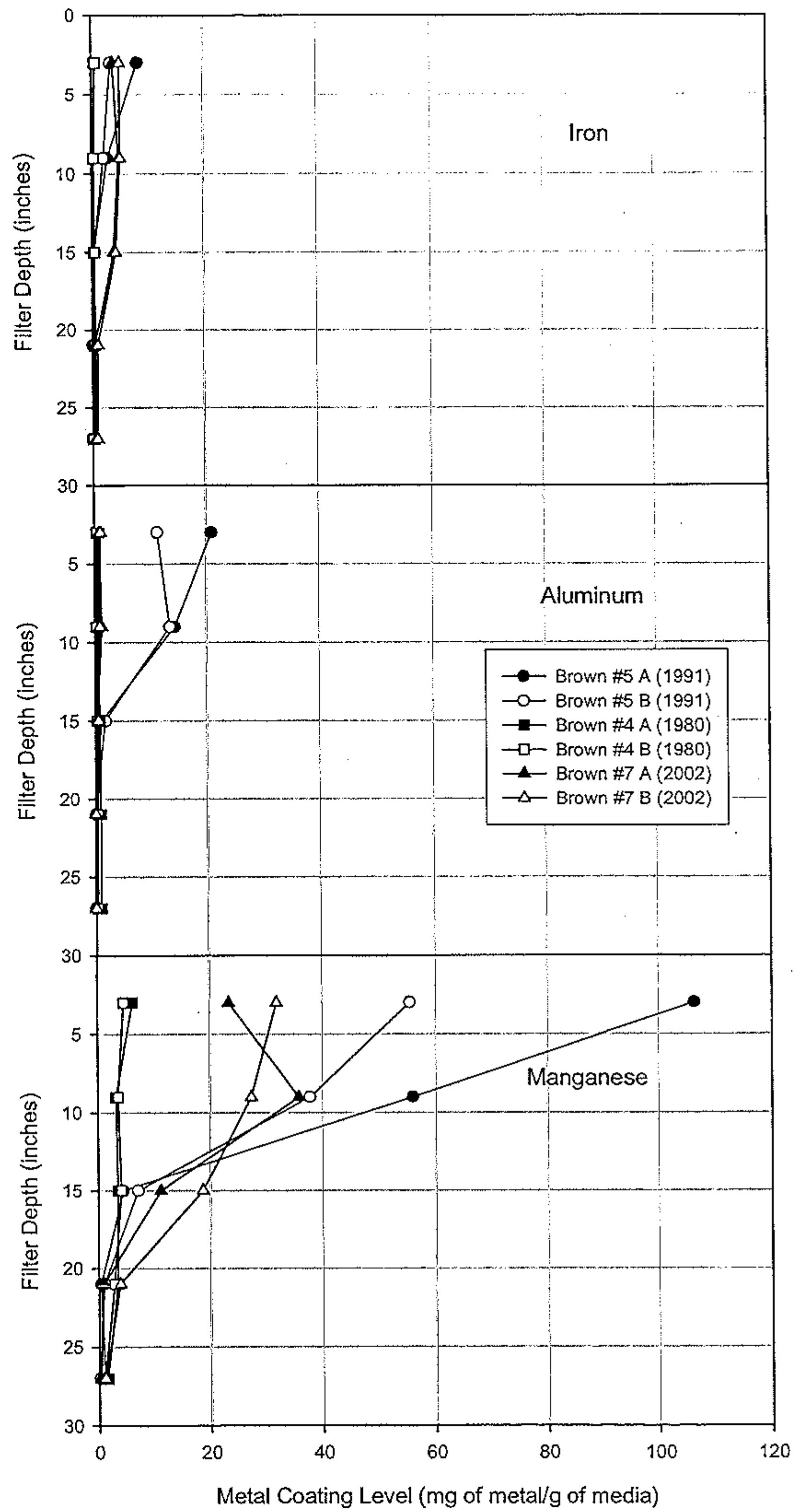

Figure 4-14 Brown Metal Coating Levels (June 1, 2005)

The metal coating results show a significant amount of difference between the filters sampled. Also, there seems to be no correlation between the amount of metal coating and the length of time the filter had been in service. In fact, the filter that had been in service for the longest period of time was shown to have the lowest amount of extractable metals. In general, the media from all filters sampled shows a substantial amount of metal coating. Further discussion of the variation in metals concentrations takes place in Section 4.2.

In the June sampling event, the average amount of Mn oxide coating in the anthracite layers for filters 4, 5 and 7 were 4.20, 44.6 and 24.7 mg Mn per gram of media, respectively. In the November sampling event, the average amount of Mn oxide coating in the anthracite layers for filters 3, 5 and 7 were 15.6, 53.8 and 6.17 mg Mn per gram of media, respectively.

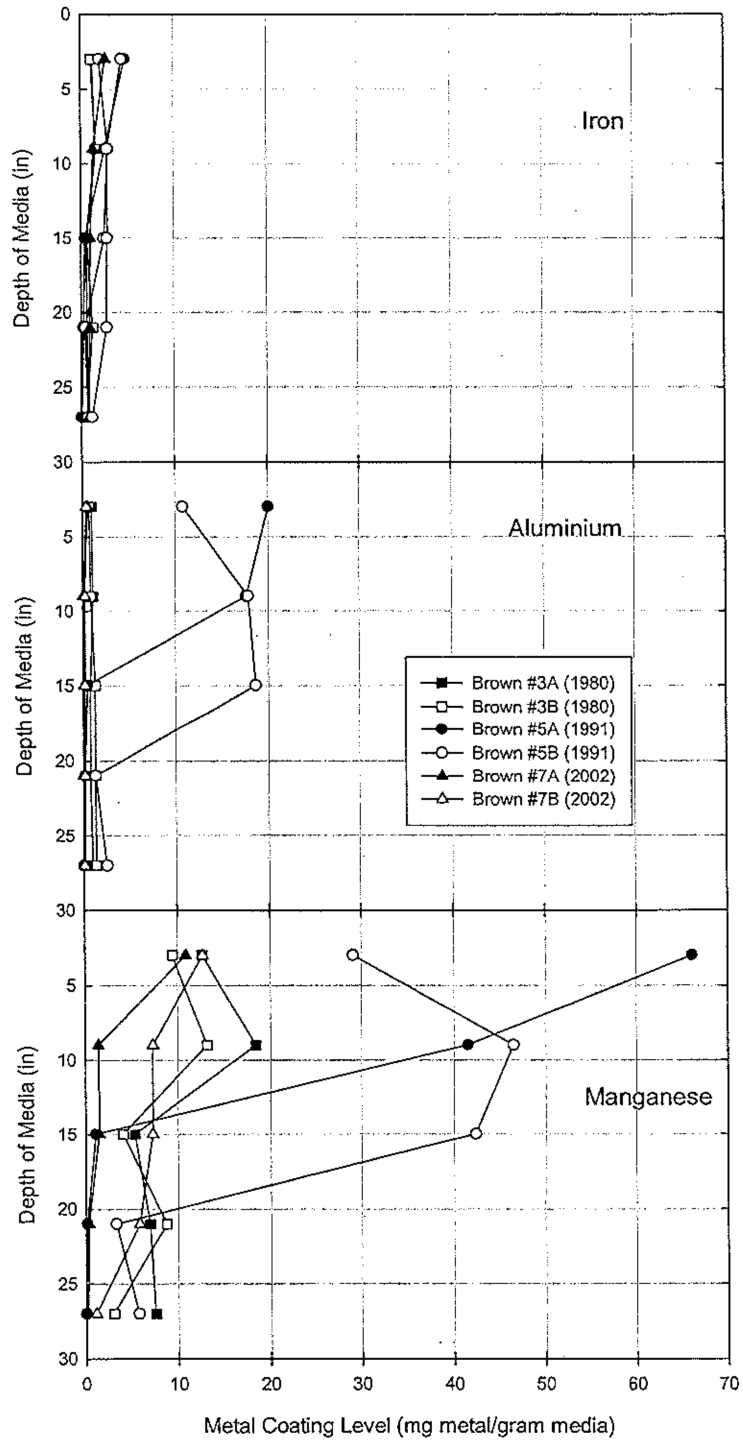

Figure 4-15 Brown Metal Coating Levels (Nov. 29, 2005)

4.1.7 Harwood's Mill WTP – Newport News, VA

4.1.7.1 Treatment Process

The Harwood's Mill WTP, located in Newport News, Virginia, treats surface water from the Chickahominy River which enters a terminal reservoir. The flow is also supplemented by five other reservoirs. The treatment plant has a capacity of 32 MGD. The plant treats is water through coagulation, flocculation, settling, intermediate ozonation, dual filtration and disinfection. Pre-oxidation, using a $KMnO_4$ dose of up to 2 mg/L is also used during periods of elevated Mn in the raw water.

The raw water at Harwood's Mill WTP is coagulated with alum. The pH of settled water varies between 5.9 and 6.3. The water is filtered through parallel dual media filters. The filter media were installed in 1989. The D_{10} of the anthracite in the sampled filter was 1.0 mm and the D_{10} of the sand was 0.50 mm.

Chlorine is used for disinfection and regeneration of oxide coated filter media. Chlorine is dosed to the water before and after filtration. The pre-filter chlorine dose varies seasonally from 2.9 to 3.6 mg/L in the summer and 0.5 and 0.9 mg/L in the winter. The chlorine dose following treatment also varies depending on the pre-filter dose. In the summer months, the post filter chlorine dose is approximately 1.0 mg/L while in the winter months this dose is between 3.4 and 4.0 mg/L.

4.1.7.2 Raw Water Quality

The raw water entering the Harwood's Mill WTP has TOC concentrations ranging from 5.5-6.3 mg/L, over 95% of which is dissolved. The average raw water pH is 6.9. The average hardness and alkalinity of the raw water are 50.4 and 34.6 mg/L (as $CaCO_3$) respectively.

Figure 4-16 shows a plot of historical Mn concentrations entering the Harwood's Mill WTP. In this plot, the manganese has been separated into total and dissolved Mn. The plot shows the typical late summer increase in Mn concentration. The average total Mn concentration during the time period was 0.19 mg/L with a maximum of 1.4 mg/L. On average, the dissolved Mn comprised 25% of the total Mn. The maximum dissolved Mn concentration was 0.45 mg/L with an average of 0.05 mg/L.

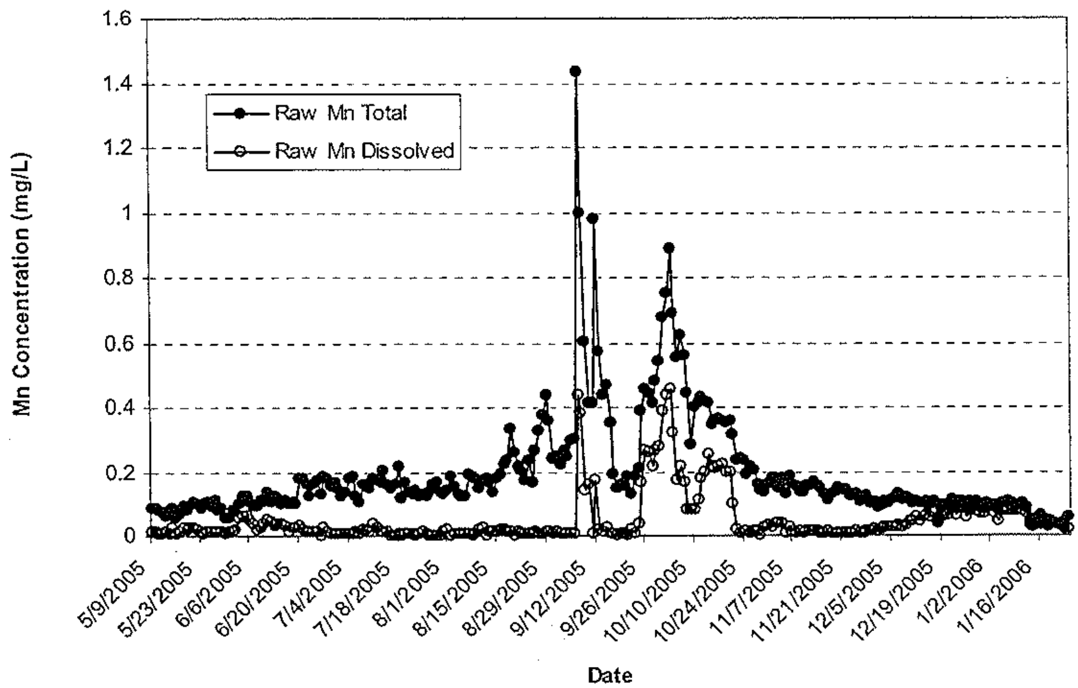

Figure 4-16 Harwood's Mill WTP Total and Dissolved Mn Concentrations (2005)

4.1.7.3 Metal Coating Levels

Media sampling at the Harwood's Mill WTP was performed on May 2, 2005, November 1, 2005 and May 9, 2006. Two cores were taken from the same filter on each sampling occasion.

The results of the metals extraction for all three sampling events are shown in Figure 4-17. As found for dual media from other facilities, the levels of extractable metals on the filter media decrease proportionally with depth through the filter. During the sampling events, the Mn, Al and Fe coating levels in the anthracite layers ranged from 20.4-40.8, 19.9-27.7 and 1.20-1.59 mg metal per gram of media respectively. Each metal showed a similar profile pattern with depth and much lower concentrations in the sand layers of the filter. The elevated Al levels may be related to the use of alum as a coagulant.

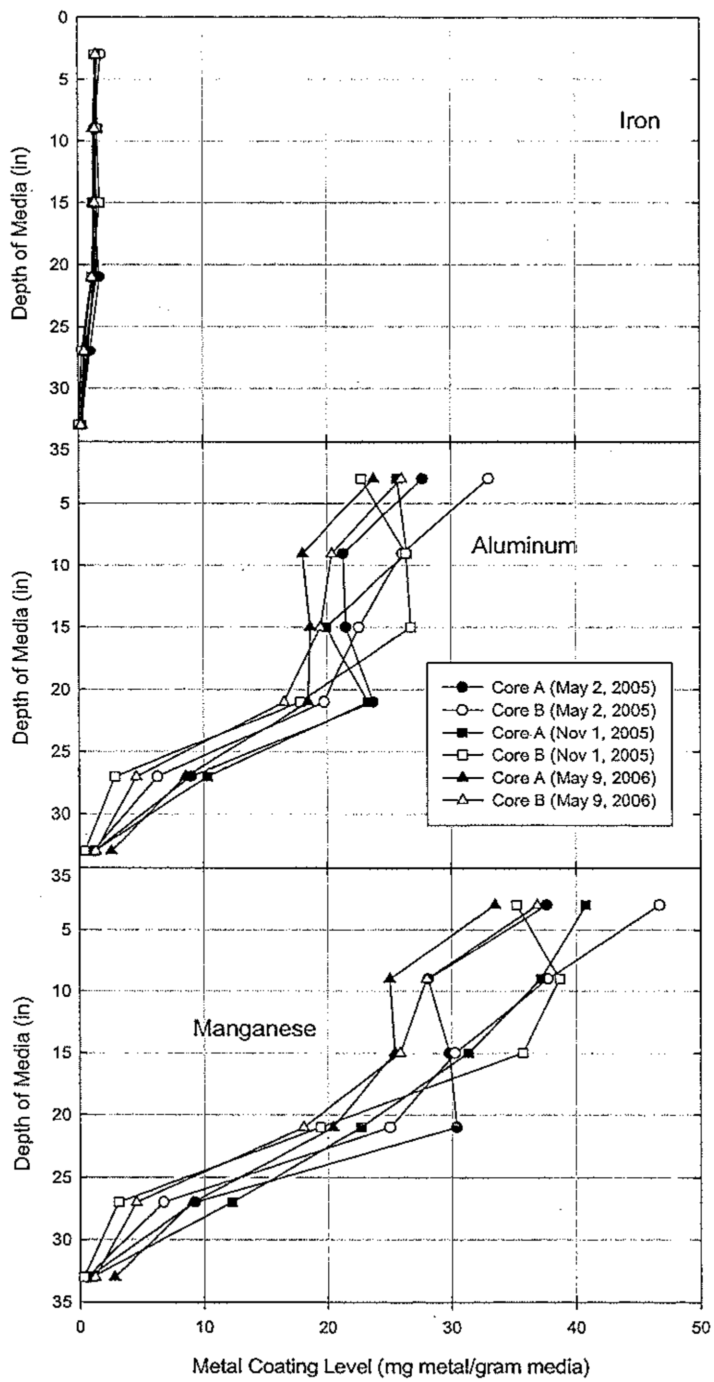

Figure 4-17 Harwood's Mill Metal Coating Levels

4.1.8 Sobrante WTP – EBMUD, CA

4.1.8.1 Treatment Process

The Sobrante WTP, operated by EBMUD, treats influent water from a local lake source. The surface water source is subject to seasonal stratification. The plant has a design capacity of approximately 20 MGD. The treatment process includes pre-oxidation with permanganate, coagulation, flocculation, plate sedimentation, intermediate ozonation, dual media filtration and disinfection. The permanganate dose ranges from 0.15 mg/L to 0.35 mg/L and does not seem to be related to raw water Mn concentrations. The raw water is coagulated with a combination of alum and cationic polymer.

The plant has four, parallel, dual media filters. The filter media were installed in 2000-2001. The D_{10} of the anthracite and sand in the sampled filter were 0.80 mm and 0.50 mm respectively. The filters are pre-chlorinated with free chlorine dosages up to 5 mg/L. The pH of filtration is typically 7.5-7.6.

4.1.8.2 Raw Water Quality

Figure 4-18 shows historical, daily raw water Mn data for the Sobrante WTP from January 2, 2005 to December 16, 2005. There is seasonal variation in the Mn concentration, however the highest concentrations occur somewhat later than typically seen, in the late fall and early winter. The maximum Mn concentration was 0.16 mg/L and the average was 0.042 mg/L. The raw water TOC ranges from 3.5 to 4.5 mg/L and contains relatively low levels of humic and fulvic materials. The average pH is 7.82. The average turbidity is 10.22 NTU. This high average value is due to high spikes in raw water turbidity. During the months of March and April, 2006, the average turbidity was 29.2 NTU.

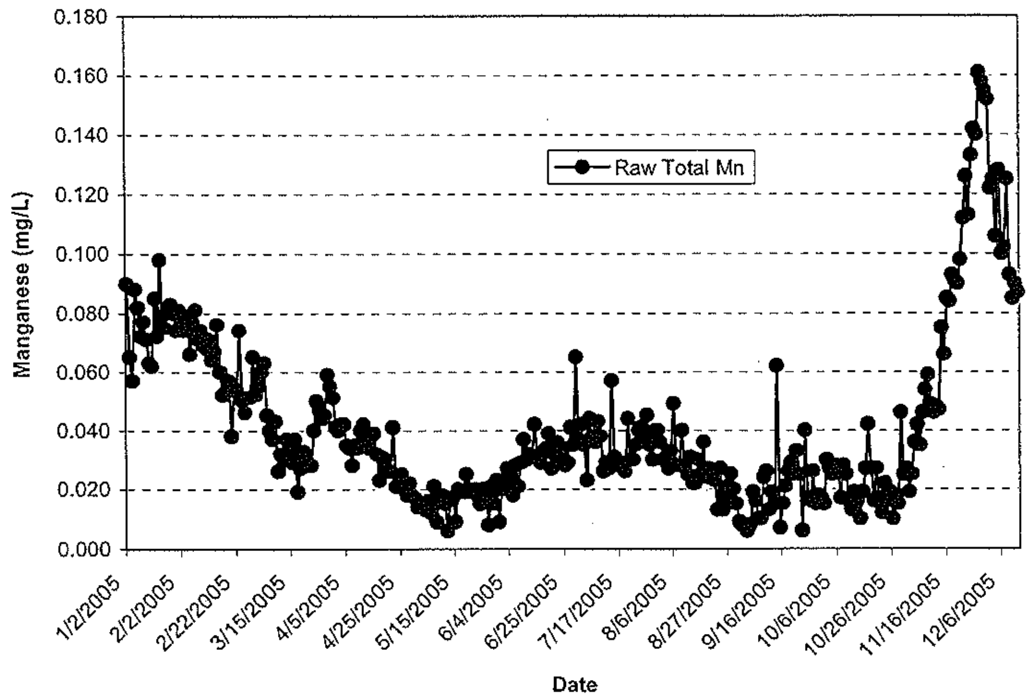

Figure 4-18 Sobrante Daily Raw Total Mn Values (2005)

4.1.8.3 Metal Coating Levels

Media sampling at the Sobrante WTP occurred on July 1, 2005 and December 6, 2005. Two cores were collected from the same filter on both dates. All media samples were extracted and analyzed for metal oxide coatings. The results for both sampling events are shown in Figure 4-19 which shows profiles of Mn, Al and Fe coating levels versus filter depth. In general, the media contained low levels of metal oxide coatings. The average Mn, Al and Fe levels in the anthracite layers were 0.65, 1.3 and 0.30 mg metal per gram of media, respectively. The low Mn levels may be attributed to the low levels of total of dissolved Mn in the raw water. Al comprised the largest amount of extractable metal, possibly because of the use of alum as a coagulant. The average Mn, Al and Fe levels in the sand layers of the media were 0.11, 0.43 and 0.38 mg metal per gram of media, respectively.

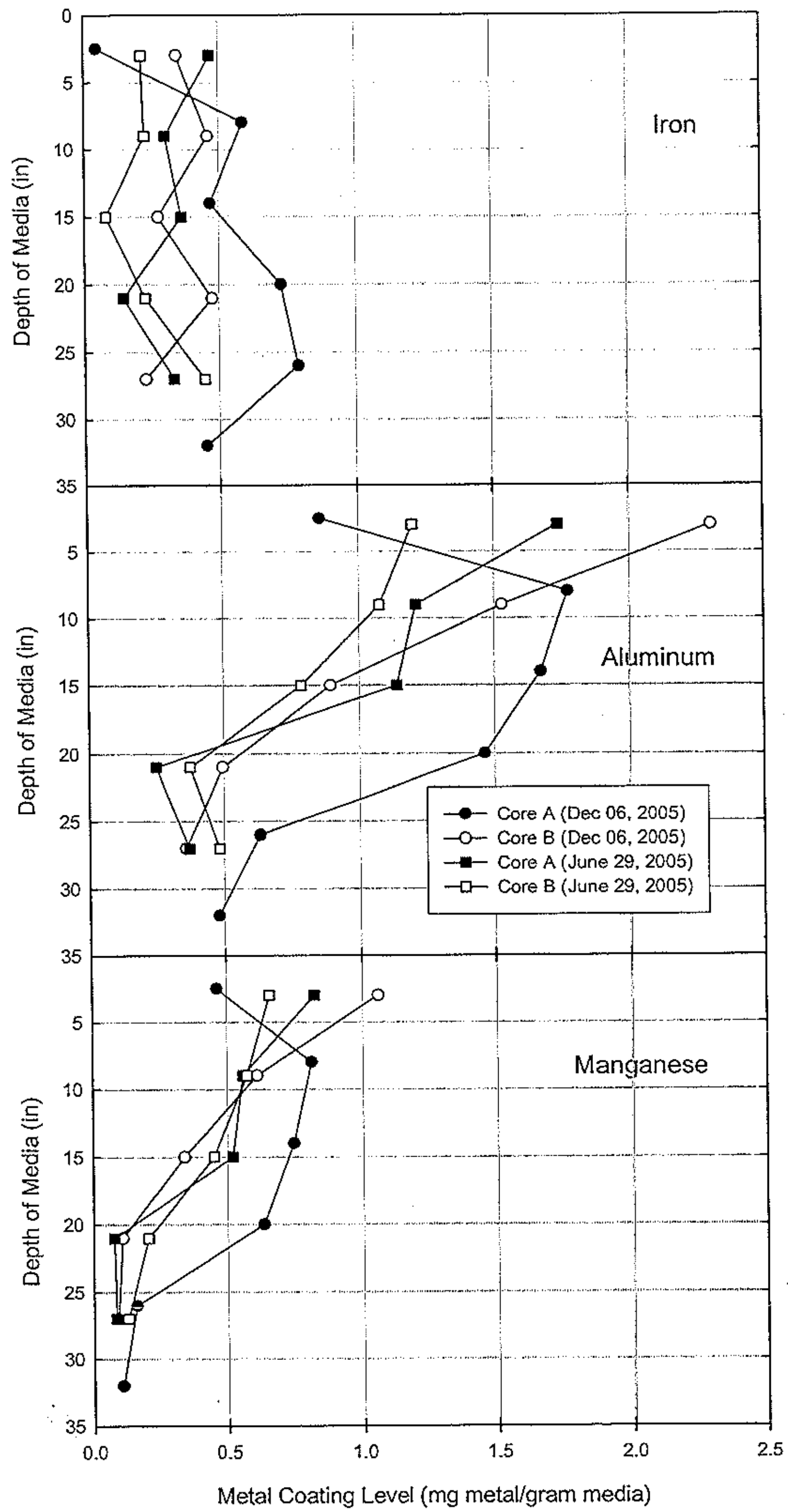

Figure 4-19 Sobrante Metal Coating Levels

4.1.9 Upper San Leandro (USL) WTP - EBMUD, CA

4.1.9.1 Treatment Process

The USL WTP treats water from a local surface water source. The overall treatment process used at the plant is the same as the process used at the Sobrante WTP. However, the plant has discontinued pre-filter chlorination for over two years and pre-oxidation is not conducted.

The USL WTP uses four, parallel dual media filters. The media in the filters were installed in 2002. The average D_{10} of both the anthracite and sand were found to be 0.60 mm. Filtration is conducted at a pH range of 7.5-7.8.

4.1.9.2 Raw Water Quality

Figure 4-20 shows historical, daily raw water Mn data for the USL WTP from April 15, 2005 to November 15, 2005. Gaps in the data indicate times when the plant was taken off-line. The maximum Mn concentration occurred in the late summer; however there is a possibility that the value is an invalid outlier. The raw water Mn levels do not appear to have typical season variation of other surface waters. The average Mn concentration was very low at 0.02 mg/L. The raw water TOC typically ranged between 4-5 mg/L. The average pH and turbidity values were 7.64 and 1.75 NTU, respectively.

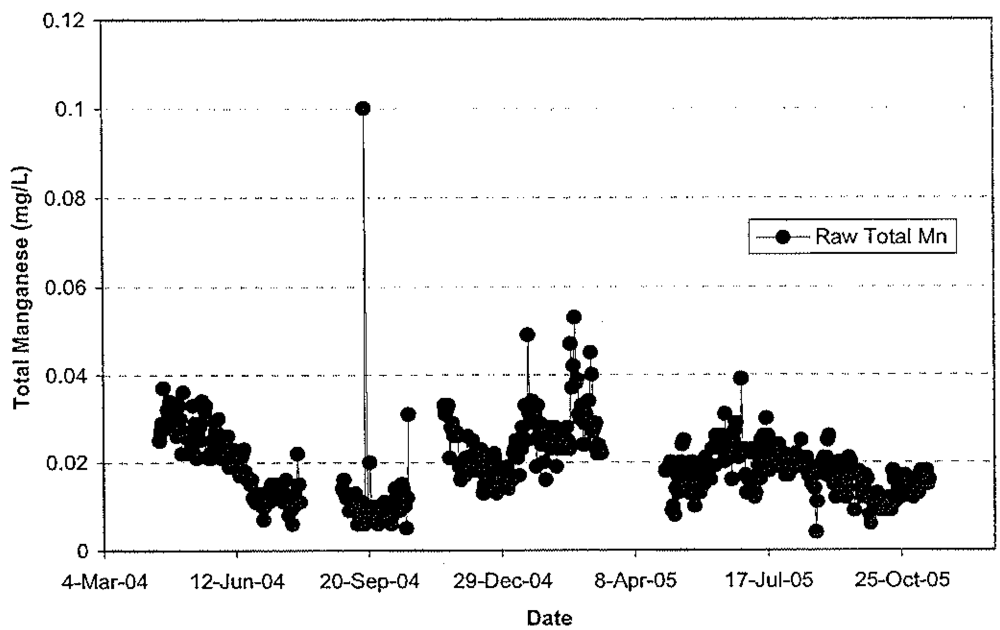

Figure 4-20 USL Daily Mn Values 2005

4.1.9.3 Metal Oxide Coating Levels

Media sampling at the USL WTP was conducted on June 27, 2005. Two cores were collected from filter 1. The media samples were extracted and analyzed for metal coatings. The results for both cores are shown in Figure 4-21 which shows the levels of Mn, Al and Fe coatings as a function of depth. The average Mn, Al and Fe amounts in the anthracite layers were 0.04, 0.46 and 0.67 mg metal per gram of media, respectively. The levels of extractable Mn on the surface are very low. This is most likely because the concentration of Mn in the raw is very low and no pre-filter chlorine was applied. Al was present in levels in the filter higher than Mn, which could be attributed to the use of alum as a coagulant. Fe was also present in levels greater than Mn which could be caused by higher Fe concentrations in the raw water.

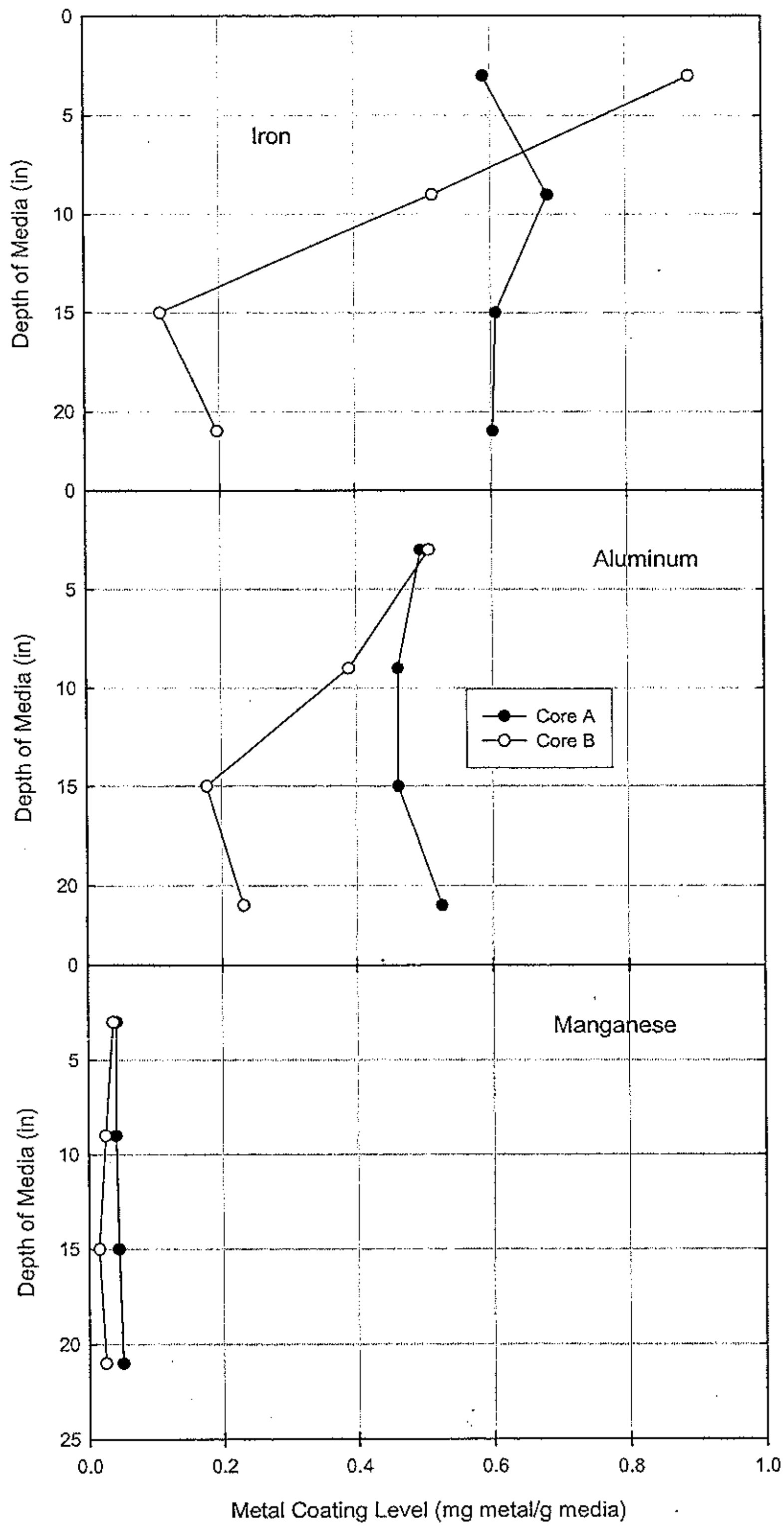

Figure 4-21 USL Metal Coating Levels

4.2 Analysis of Media

This part of Chapter 4 contains an in-depth analysis of the results from the media characterization. Topics discussed in this section include the variability of the Mn coating, the ratios of metals that comprise the media coating, the surface area of metal coated media, and the adsorption onto of metal coated filter media. The section concludes with a discussion of the impact of pre-filter chlorine on media characteristics and overall Mn removal at the lab and full scale.

4.2.1 Metal Coating Level Variability

The variability of the metal coating found on media samples is discussed in this section. The focus is on statistical and temporal variability, as well as on the impact of raw water quality, media type, and media depth on coating level.

4.2.1.1 Statistical Variability

Duplicate extractions were conducted for each sub-sample of media from each filter core. In the metal coating versus depth plots shown in Section 4.1, the duplicate results were averaged, giving a single value for each depth sub-sample.

In order to help describe the statistical variability of metal coating levels, the difference between the two duplicate values was calculated and normalized by dividing by the average value. This fractional variability was plotted versus the average metal coating level. The resulting plot, shown in Figure 4-22, helps quantify the statistical variability of the oxide coating results. Each point on the figure represents the fractional variability between two duplicates from the same sub-sample.

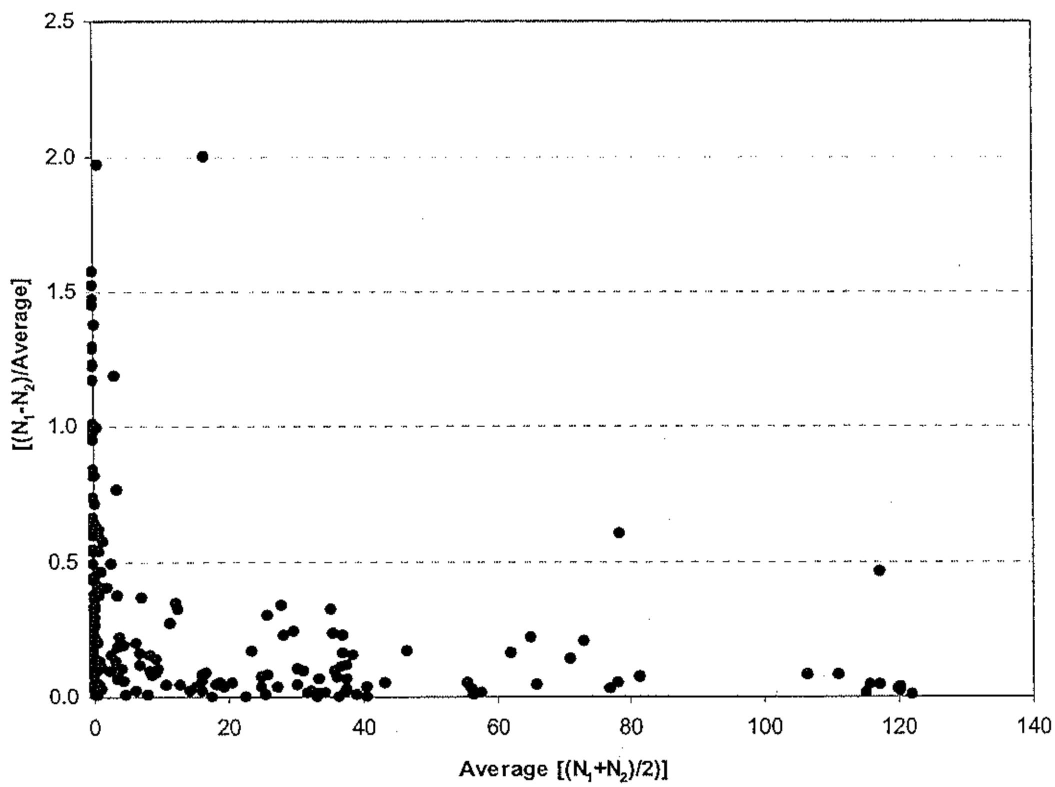

Figure 4-22 Fractional Variability of Duplicate Mn Oxide Coating Results

Figure 4-22 shows that the fractional variability of the duplicate oxide coating varies from a fraction of 2 (200%) at low Mn coating levels to approximately 0.2 (20%) at higher Mn coating levels. For samples with an average coating greater than 0.1 mg of Mn per gram of media, the average variability between two results from the same sub-sample was 22.3%. This indicates that there is a large amount of variability within an individual sub-sample. This variability is to be expected due to the environment from which the sample was taken, and the relatively low amount of sample (~1 gram dry) analyzed per result. Figure 4-22 also shows that the higher the concentration of Mn oxide on a filter media, the less variability there is between duplicate measurements. This is to be expected as the lower concentrations, which are closer to the detection limits of the analytical methods described in Chapter 3, are more difficult to measure. Accordingly, there is more statistical variability in the results for low Mn levels.

On August 16, 2005, at the Trap Falls WTP, another effort to quantify statistical variability was conducted by taking numerous cores from the same filter during a single sampling event. Six cores were collected, and each was delineated into sub-samples and analyzed for metal coating levels. The results, presented in Figure 4-23, show the range of variability of the Mn oxide coating from this filter. Of the six cores, one core, core A, consistently had higher Mn coating levels than the other five. This indicates that the metal oxide coatings are somewhat heterogeneous within a filter.

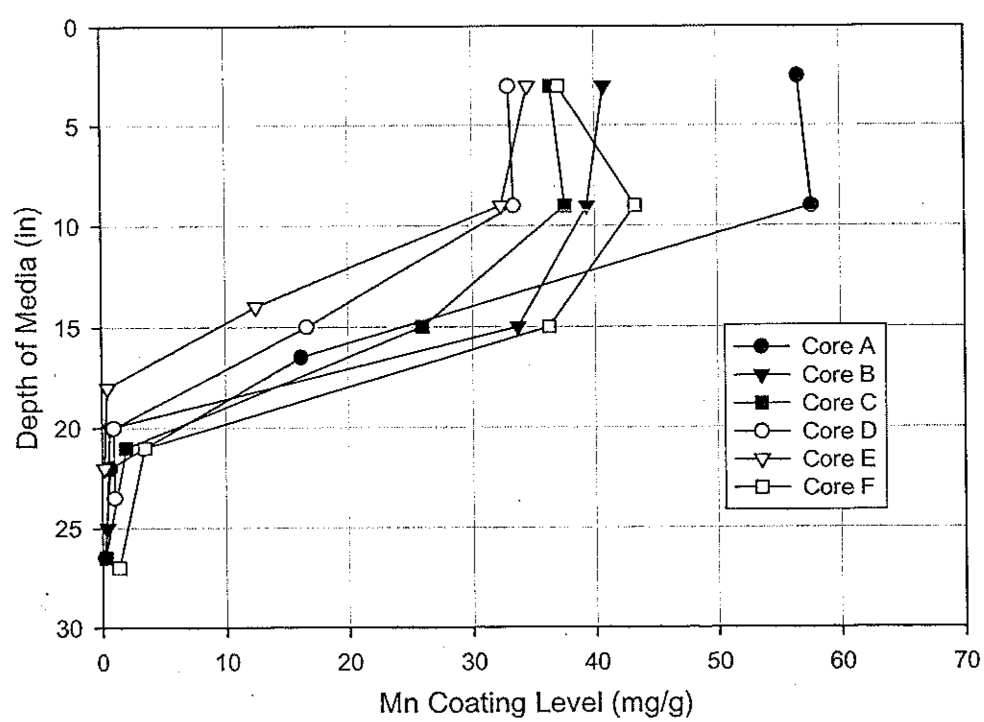

Figure 4-23 Trap Falls Mn Coating Levels (6 Cores – Aug 16, 2005)

The variability in coating level can also be assessed in the duplicate cores taken from filters at other WTP. In general, duplicate cores were taken from each filter sampled. Each core was individually measured for Mn oxide coating level. The fractional variance between the results for each duplicate core sub-sample was quantified by taking difference of the duplicate results and then dividing by the value of the average. This fractional variability was plotted versus the average coating level. The results in Figure 4-24 show the variability of metal coating levels between two cores, which help quantify the variance of metal coating levels within a filter. The figure shows that the average variance between two cores with a coating of greater than 1 mg Mn per gram of media is 33.9%. This high difference describes a high degree of variance between two cores and also indicates the heterogeneous nature of the metal coatings in the filters studied.

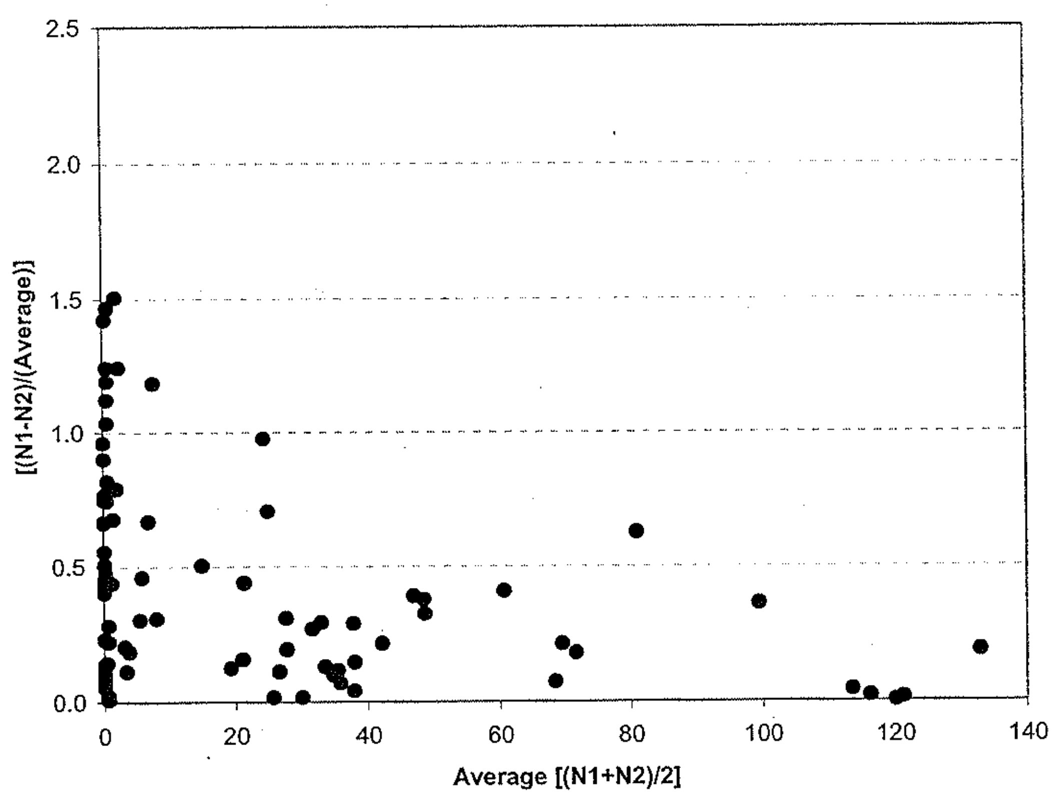

Figure 4-24 Fractional Variability of Duplicate Core Mn Oxide Coating Results

4.2.1.2 Temporal Variability

The temporal variability of the metal coating levels was also assessed. Sampling events were conducted at the Harwood's Mill WTP in VA and the Warner WTP in CT at various intervals to determine if the amount of Mn on the filter media changed with time. Coating levels might change due to variations in raw water Mn over time combined with losses due to backwashing. Oxide coating level results from the sampling at Harwood's Mill WTP are shown in Figure 4-25. Sampling was taken at three different times; May 2, 2005, November 1, 2005 and May 9, 2006. The results show no pattern of temporal variability in Mn oxide coating level over the time period studied. The Mn oxide coating did not increase over time, but appeared to slightly decrease from May 2, 2005 to May 9,

2006. However, the temporal variability was within the approximately 20% statistical variability between samples from one media sub-sample.

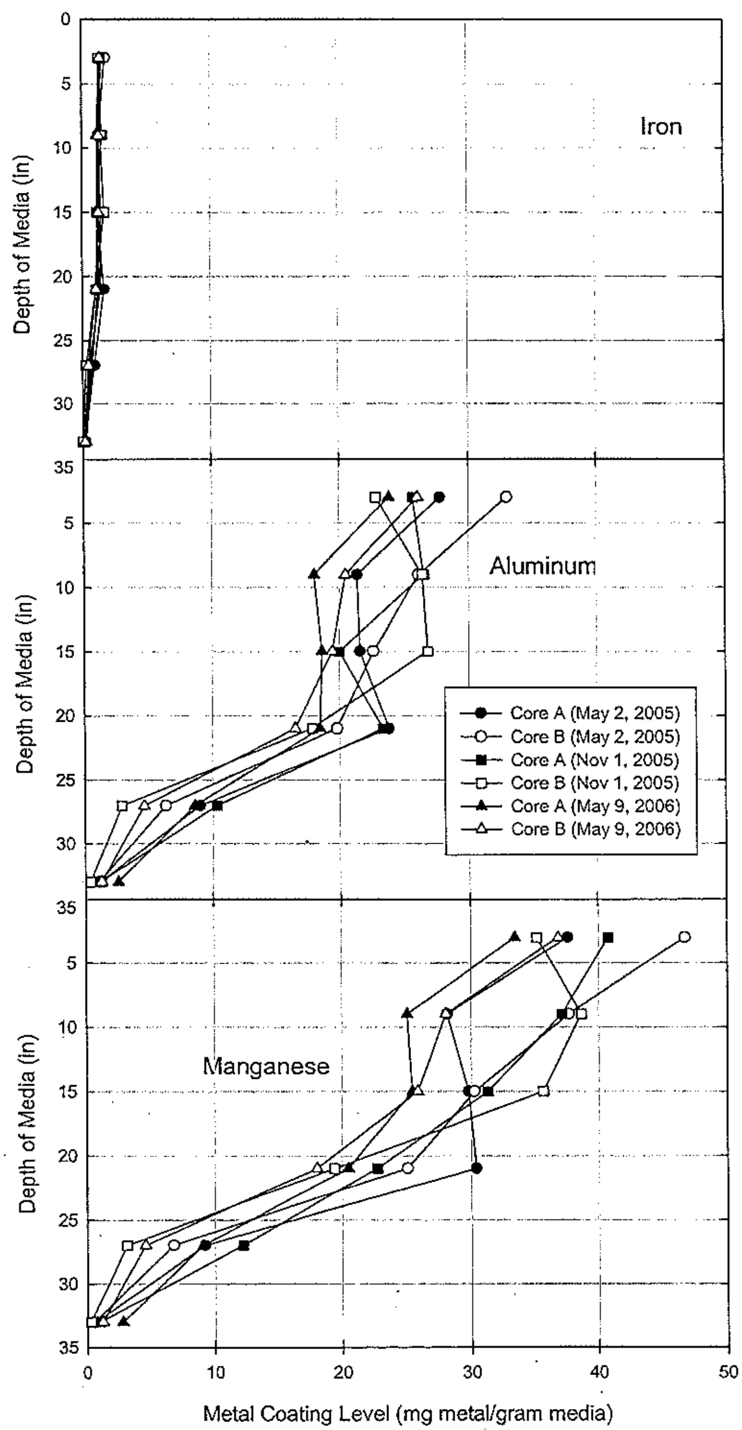

Figure 4-25 Newport News Metal Coating Levels

A series of four sampling events occurred at the Warner WTP. Results are shown from the sampling that occurred at Warner WTP on January 12, 2005 and January 10, 2006. Results are shown in Figure 4-26. The results show that during the year between the two sampling events there was a slight increase in Mn coating on filters 7 and 9. Also, the Mn profiles taken in January 2006 indicate that higher levels of Mn coating were found at greater depths in both filters than compared to January 2005. This increase in coating at lower depths in the filter could be caused by more Mn being adsorbed subsequently oxidized in the anthracite layers during the time span between sampling. Filter 9 was not receive pre-filter chlorine continuously during this time, however during the seasonal increase in raw water Mn at the Warner WTP filter 9 was receiving pre-filter chlorine.

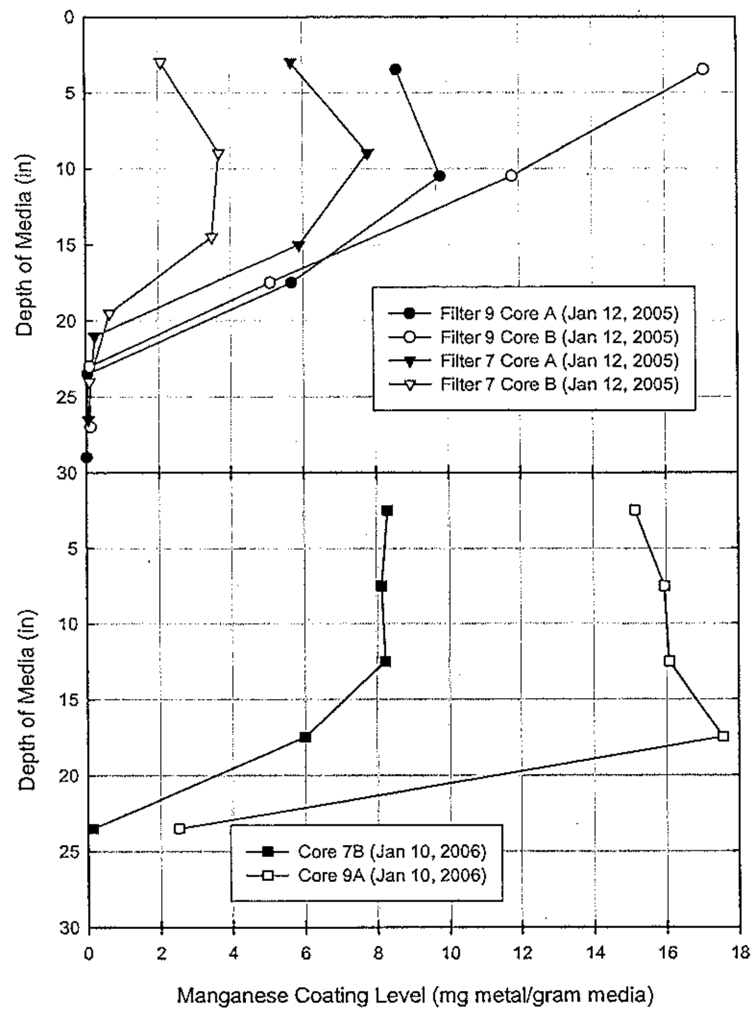

Figure 4-26 Warner Mn Coating Levels (Jan 2005 and Jan 2006)

4.2.1.3 Coating Variability and Raw Water

A qualitative assessment of the relationship between the amount of Mn coating on a sample of filter media and the amount of raw water Mn that enters the treatment plant was conducted. Table 4-3 shows the average raw water Mn and average Mn oxide coating levels for each participating WTP. In general, the plants which received higher amounts of raw water Mn had higher amounts of Mn oxide coating than plants which received lower levels of Mn in the raw water. Plants with relatively high raw water Mn and high levels of Mn oxide coating include the Brown, Carno, Canteraf and Harwood's Mill WTP. Plants with relatively low levels of raw water Mn and low levels of Mn oxide coating include the Warner, Sobrante and USL WTP. Many factors can affect the amount of Mn in the raw water that is initially adsorbed, remains adsorbed and subsequently oxidized on the media. Some of these factors include the fraction of raw water Mn that is dissolved, the use of a pre-oxidant in the treatment process, the pH of filtration, the pre-filter chlorine dose, the use of a ferric coagulant, the rate of filter backwash, and use of air scour in filter backwash. One or several of these operational parameters are changed at many WTPs during the life span of the filter media. Also, filters will be sometimes topped off with new media to replace lost media. This practice makes the filter media age difficult to define. Without clear knowledge of all these factors it is difficult to draw clear conclusions between the amount of Mn coating and raw water Mn levels beyond this point.

Table 4-3 Average Raw Water Mn and Average Mn Coating Level

Plant	Average Raw Mn (mg/L)	Average Coating (mg Mn/g media)
Trap Falls	0.082	21
Warner	0.036	6.4
Stamford	0.042	28.8
Canteraf	0.068	74
Carno	0.240	120
Brown	0.230	15.3
Harwood's Mill	0.190	21.9
Sobrante	0.042	0.44
USL	0.020	0.04

A quantitative mass balance relating yearly Mn load to the amount of Mn extracted from filter media was attempted by Bouchard (2005) for several AWC plants. Overall, Bouchard found that the higher the Mn yearly load at a WTP, the more Mn was found on the filter media of that WTP. The time of service of the media also played a role. Older media generally had more Mn coating than younger media. No plants studied by Bouchard (2005) used a pre-oxidant or intermediate ozone which may impact that results of such a mass balance.

4.2.1.4 Coating Variation with Media Material

The results of the metal coating levels show that the amount of metal that can be present on a sample of filter media is independent of the type of media material. High levels of metal oxides have been found on both anthracite and sand media, as have low levels. For example, the highest amount of Mn coating found during this study was from the sand media of the second stage filter from the Carno WTW at approximately 120 mg Mn per gram of media on average. However, anthracite from the Trap Falls WTP had a large amount of Mn oxide coating at 21 mg Mn per gram of media. Sand has been found with very low coating in the bottom layers of several dual media filters as well as from the first stage filters at the Carno WTW. Anthracite at the USL WTW was found to have on average 0.04 mg Mn per gram of media. A summary of average coating levels found on each type of media studied is shown in Table 4-4.

Table 4-4 Mn Coating Levels for Each Media Type

Dual Media Plants		
Plant Name	**Media Type**	**Ave. Mn Coating (mg Mn/g media)**
Trap Falls	Anthracite	34.6
	Sand	0.98
Warner	Anthracite	11
	Sand	1.14
Brown	Anthracite	24.5
	Sand	1.45
Harwood's Mill	Anthracite	30.8
	Sand	1.09
Sobrante	Anthracite	0.64
	Sand	0.13
USL	Anthracite	0.04
	Sand	0.03
Sand Media Plants		
Plant Name	**Media Type**	**Ave. Mn Coating (mg Mn/g media)**
Canteraf	Stage 1	0.09
	Stage 2	74.1
Carno	Stage 1	0.14
	Stage 2	121
Stamford	Stage 1	28.8
	Stage 2	0.01

In several instances, in a dual media filter, the top anthracite layers of the filter have had significantly more coating than the bottom sand layers. However, this is not due a difference between anthracite and sand with respect to Mn uptake. Any filter media that is positioned at the top of the filter will develop the most coating. More Mn is removed and thus oxidized on the surface of the top layers of filter media because the concentrations of Mn^{+2} and free chlorine are the greatest. In instances of a dual media filter, if the anthracite was replaced with a larger, less dense, media then this media would have higher levels of Mn coating than the sand layers below. For example, relatively high levels of Mn oxide coating have been found on Pyrolusite media used in a manganese contactor and even on a GAC media (Knocke, 2006).

4.2.1.5 Coating Variation with Media Depth

Many filter cores exhibit a metal coating depth profile which is greatest near the top of the filter, then decreases through the depth of the filter. To further analyze this profile, and make comparisons between cores from different plants, the relative coating for each profile was calculated by normalizing the coating level of each sub-sample from a core by the highest coating level obtained in that core. This was done for one core from each of the Warner, Trap Falls, Brown and Harwood's Mill WTPs. These plants represent the four WTPs that participated in this study that have significant metal oxide coating levels on dual media. The results are shown in Figure 4-27.

Figure 4-27 shows that in all the filter profiles, most of the Mn coating occurs in the upper 50% of the media. In the lower 25% of media, there is less Mn coating, and in the final 6 inches of media, very little Mn coating is seen. This profile is caused because of the uniformity of media within an individual, homogenous layer which develop a uniform coating level. The middle of the filter depth, referred to as the mixed layer, contains a mixture of anthracite and sand and the higher and lower Mn coating levels, creating a moderal level of coating relative to the anthracite and sand layers, respectively.

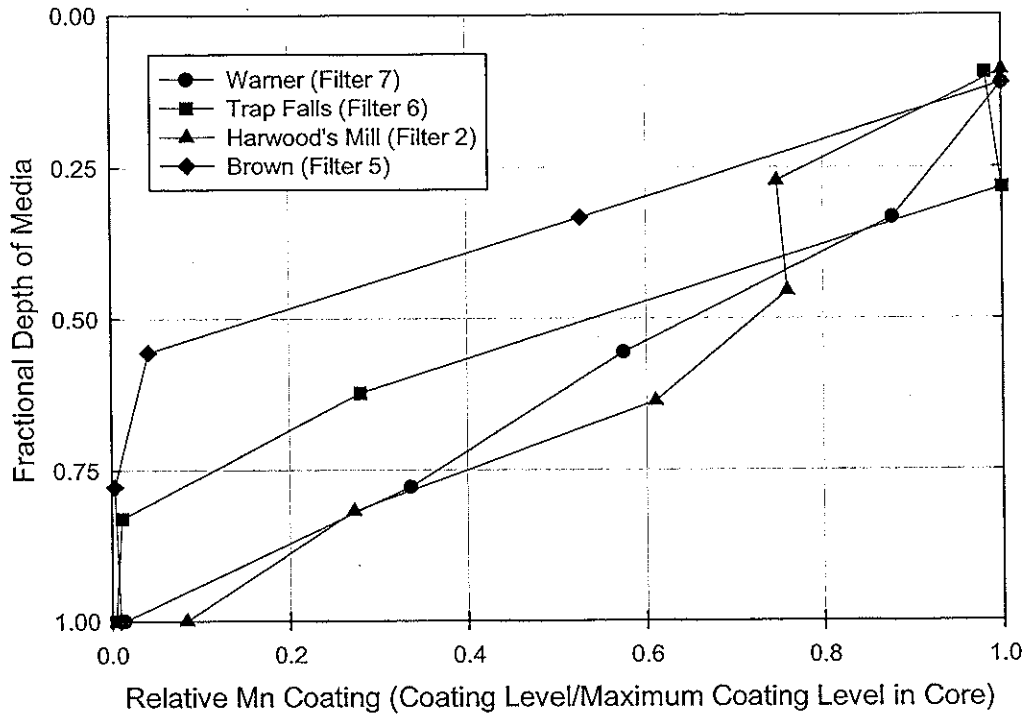

Figure 4-27 Relative Mn Coating vs. Media Depth

4.2.2 Metal Ratios

As discussed previously in Chapter 4, in the majority of plants sampled, the depth profiles of each metal extracted from the media were very similar. The example previously discussed was for the second stage filters at the Canteraf WTW, shown in Figure 4-8. The results show that the pattern of variability in the Mn coating profile is also reflected in the profiles of the other metals (Fe, Al and Ca). For example, core B from Figure 4-8 has more extractable Mn than core A, except for the sub-sample taken from a depth of 12 inches. This sub-sample has a lower amount of Mn coating than the same sub-sample from core A. This specific pattern is also reflected in the Fe, Al and Ca profiles, where all three plots show the same decrease in the metal coating levels for core B at a depth of 12 inches. This pattern of similar profiles for all metals was unexpected. Further study of this phenomenon would be appropriate.

A method to examine patterns of metal coating levels is through the ratios of the extracted metals present in an oxide coating. To accomplish this, the level of extracted metal was normalized by dividing by the amount of extractable Mn on the same filter media sample.

Table 4-4 shows the metal molar ratios for both cores taken from the Canteraf 2nd stage filter. The results show that Fe, Al and Ca levels were lower than the Mn coating level and that eh metal ratios are very consistent with little variation with depth. On average, the Al level was 21% of the Mn level, the Fe level was 59% of the Mn level and the Ca level was 30% of the Mn level. Aluminum is the only metal that Canteraf does not directly add as part of the treatment process as an iron based coagulant is utilized. Recall that lime is added between the 1st and 2nd stage filters to increase pH. Analysis of the metals rations was only conducted on the 2nd stage filters of the Canteraf and Carno WTW because of the very low levels of Mn in the 1st stage filters.

Table 4-4 Metal Ratios for Canteraf 2nd Stage Filter

Canteraf 2nd Stage	Core A (mol/mol)			Core B (mol/mol)		
Sample	Fe:Mn	Al:Mn	Ca:Mn	Fe:Mn	Al:Mn	Ca:Mn
1	0.60	0.25	0.36	0.63	0.17	0.27
2	0.61	0.37	0.33	0.68	0.18	0.27
3	0.57	0.22	0.33	0.54	0.14	0.31
4	0.55	0.21	0.30	0.64	0.16	0.27
5	0.51	0.16	0.27	0.61	0.20	0.29

Table 4-5 lists the metal molar ratios for the Carno 2nd stage filter. Again, the ratios are consistent with depth. In the case of Carno, alum is used as a coagulant. Compared to the Canteraf WTW, Carno has a much lower Fe:Mn ratio and much higher Al:Mn ratio. On average, the Fe level is 8% of the Mn level, the Al level is 111% of the Mn level, and the Ca level is 45% of the Mn level. The elevated level of Al is probably due to the use of alum at Carno versus ferric sulfate at Canteraf. The ratio of Ca to Mn of 45% for Carno is higher than the 30% Ca to Mn ratio at Canteraf.

Table 4-5 Metal Ratios for Carno 2nd Stage Filter

Carno 2nd Stage	Core A (mol/mol)			Core B (mol/mol)		
Sample	Fe:Mn	Al:Mn	Ca:Mn	Fe:Mn	Al:Mn	Ca:Mn
1	0.08	1.08	0.53	0.08	1.10	0.40
2	0.07	1.03	0.45	0.08	1.33	0.44
3	0.08	1.07	0.45	0.07	1.05	0.49
4	0.08	1.15	0.45	0.08	1.16	0.41
5	0.08	1.08	0.43	0.07	1.06	0.47

Another metals ratio comparison, taken from the August 17, 2005 and January 10, 2006 sampling events at the Warner WTP, is shown in Table 4-6. Only the anthracite layers of the filter are included in the discussion; in the lower sand layers, the ratios are erratic due to low levels of metal oxide coating. For filter 7 (Core 7C and 7B), more coating was found for the August 17, 2005 sampling event than for the January 10, 2006 sampling event. However, the Fe:Mn and Al:Mn ratios for the two sampling events are practically identical. In the August sampling event the level of Fe was 15% of the Mn level, and the Al level was 204% of the Mn level. In the January sampling event, the level of Fe was 13% of the Mn level and the Al level was 211% of the Mn level. In filter 9 (cores 9C and 9A), the metal ratios are the same for the two sampling months even though pre-filter chlorination had not been practiced for this filter between the two different (August, January) sampling events. The results show that even with changes in levels of metal coatings, the ratios between the metals remained constant. The consistency of the metals ratios in spite of variability in overall Mn coating was unexpected.

Table 4-6 Warner Metal Ratios

Average Depth	Core	Mn Coating (mg/g)	Fe Coating (mg/g)	Al Coating (mg/g)	Fe:Mn Molar Ratio	Al:Mn Molar Ratio
August 17, 2005 Results						
2.5	7C	10.8	1.33	10.6	0.12	2.00
7.5	7C	9.46	1.31	9.31	0.14	2.00
12.5	7C	6.20	1.15	6.44	0.18	2.11
17.5	7C	3.62	1.04	4.14	0.28	2.33
22.5	7C	0.150	0.260	1.02	1.70	13.79
3.5	9C	14.2	1.61	13.9	0.11	1.99
10.5	9C	12.8	1.47	12.3	0.11	1.96
17.5	9C	6.71	1.69	6.81	0.25	2.07
22.5	9C	0.162	0.203	1.00	1.23	12.57
27	9C	0.275	0.425	1.09	1.52	8.10
January 10, 2006 Results						
2.5	7B	8.30	1.09	8.54	0.13	2.09
7.5	7B	8.14	1.08	8.47	0.13	2.12
12.5	7B	8.22	1.15	8.54	0.14	2.11
17.5	7B	6.00	0.988	6.52	0.16	2.21
23.5	7B	0.127	0.134	1.03	1.04	16.58
2.5	9A	15.1	1.56	15.9	0.10	2.14
7.5	9A	16.0	1.77	16.9	0.11	2.15
12.5	9A	16.1	1.66	17.0	0.10	2.16
17.5	9A	17.6	1.79	18.4	0.10	2.13
23.5	9A	2.52	0.613	3.25	0.24	2.62

Results for metals ratios for the May 2, 2005, November 11, 2005 and the May 6, 2006 filter media sampling events at the Harwood's Mill WTP are shown in Table 4-7. Only results for the anthracite layers were averaged and discussed. The Fe level was 5% of the Mn level for all three sampling events. The Al levels were 151%, 153% and 157% for the May 2, 2005, November 11, 2005 and the May 6, 2005 sampling events, respectively. The ratios of both Fe and Al show great consistency. The higher ratio of Al to Mn versus Fe to Mn is most likely caused by the use of alum as a coagulant.

Table 4-7 Metal Ratios for Harwood's Mill WTP

Average Depth (in)	Core	Mn Coating (mg/g)	Fe Coating (mg/g)	Al Coating (mg/g)	Fe:Mn Ratio	Al:Mn Ratio
May 02, 2005 Results (all ratios = mol/mol)						
3	A	37.7	1.54	27.8	0.04	1.50
9	A	28.1	1.37	21.4	0.05	1.55
15	A	29.8	1.28	21.6	0.04	1.47
21	A	30.4	1.72	23.8	0.06	1.59
27	A	9.25	0.984	9.03	0.10	1.99
33	A	0.675	0.218	1.20	0.32	3.61
3	B	46.7	1.84	33.0	0.04	1.44
9	B	37.7	1.34	26.1	0.04	1.41
15	B	30.3	1.51	22.6	0.05	1.52
21	B	25.0	1.48	19.8	0.06	1.61
27	B	6.78	0.568	6.33	0.08	1.90
33	B	0.539	0.228	1.09	0.42	4.12
November 11, 2005 Results						
3	A	40.8	1.44	25.7	0.03	1.28
9	A	37.2	1.59	26.5	0.04	1.45
15	A	31.3	1.19	20.0	0.04	1.30
21	A	22.7	1.38	23.3	0.06	2.09
27	A	12.3	0.735	10.4	0.06	1.72
33	A	0.975	0.214	1.23	0.22	2.57
3	B	35.2	1.33	22.8	0.04	1.32
9	B	38.7	1.51	26.4	0.04	1.39
15	B	35.7	1.76	26.8	0.05	1.53
21	B	19.4	1.11	17.8	0.06	1.87
27	B	3.14	0.286	2.91	0.09	1.89
33	B	0.310	0.028	0.438	0.09	2.88
May 09, 2006 Results						
3	A	33.5	1.45	23.8	0.04	1.45
9	A	25.0	1.20	18.1	0.05	1.47
15	A	25.4	1.24	18.7	0.05	1.49
21	A	20.5	1.25	18.5	0.06	1.84
27	A	9.11	0.816	8.60	0.09	1.92
33	A	2.80	0.298	2.59	0.10	1.88
3	B	36.9	1.44	26.1	0.04	1.44
9	B	28.0	1.36	20.5	0.05	1.49
15	B	25.9	1.33	19.5	0.05	1.53
21	B	18.0	1.09	16.5	0.06	1.87
27	B	4.55	0.465	4.63	0.10	2.07
33	B	1.22	0.199	1.31	0.16	2.20

The metal ratios for each treatment plant show an unexpected consistency over time and between samples. In general, the relative amount of each metal (Al, Fe or Ca) can be explained by the addition of metals in a treatment process or the presence of the metals in the raw water. However, the mechanisms for Al and Fe uptake are not well understood, and the consistency between them can not be readily explained.

4.2.3 Surface Area of Oxide Coated Filter Media

As described previously in Chapter 2, prior characterizations of oxide coated filter media have found the nature of the oxide coating to be rough and porous. The internal porosity of the surface coatings contributes a significant amount of surface area to the filter media. Merkle et al. (1997) measured the surface area of oxide coated filter media and developed a correlation between surface area and Mn coating level; the results are shown in Figure 2-4.

In this study, the work of Merkle et al. (1997) was extended by analyzing numerous samples for metal coating and surface area. Many samples analyzed in this study were from utilities that did not participate in the Merkle publication. More samples, with a greater range in oxide coating level, were available for this study than was available to Merkle. Table 4-8 shows the results of the surface area analysis and Mn coating level. A correlation between surface area and extractable Mn level is shown in Figure 4-28.

Table 4-8 Surface Area and Mn Level

Sample Name	Surface Area (m^2/g)	Coating Level (mg/g)
Durham 1st Layer	92	106
Durham 1st Layer B	91	106
Durham 2nd Layer	47	56.1
Durham 3rd Layer	2.6	4.50
Durham 4th Layer	1.9	0.400
Durham 5th Layer	2.0	1.00
USL Top Layer	1.2	0.040
Sobrante Top Layer	2.2	0.800
Newport News 1st Layer A	53	37.2
Newport News 1st Layer B	54	37.2
sTrap Falls 1st Layer	55	35.8
Stamford Stage 1	37	28.8
Trap Falls 2nd Layer	35	25.4
Warner Filter 9 Top Layer	31	15.1
Carno 2nd Stage 1st Layer	7.3	121
Carno 1st Stage 1st Layer	2.9	0.166
Cantref 2nd Stage 1st Layer	4.7	65.2
Cantref 1st Stage 1st Layer	1.9	0.065

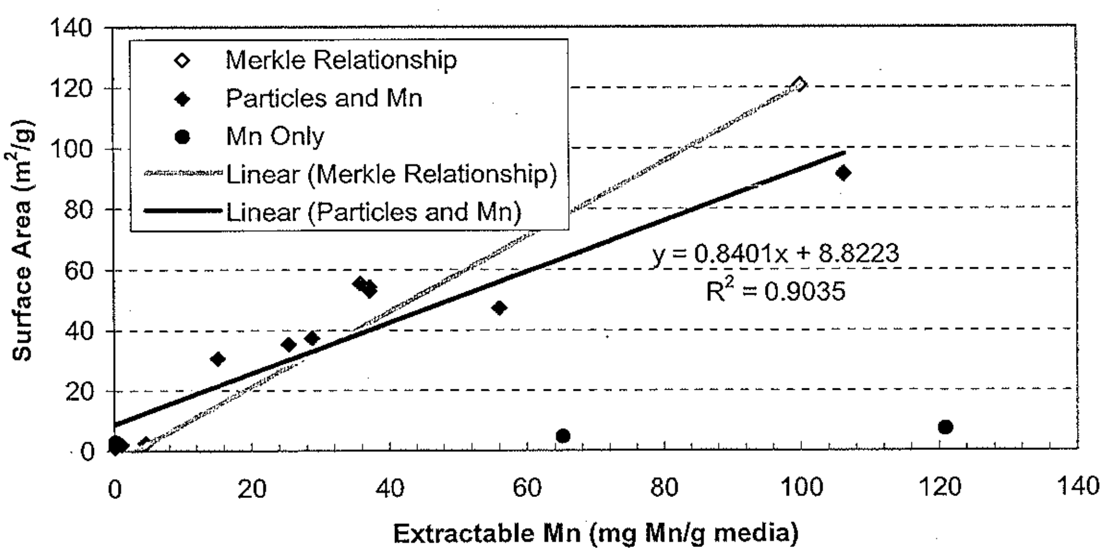

Figure 4-28 Surface Area and Coating Level Correlation

The results in Table 4-8 are for both anthracite and sand media types. The Mn level of the samples ranged from 0.1 mg Mn per gram of media to 120 mg Mn per gram of media while the surface area ranged from 1.2 m^2 per gram to 106 m^2 per gram. The surface area was proportional to Mn coating level regardless of media type. The measured surface areas are orders of magnitude greater than calculated external surface areas of 0.002 and 0.004 m^2 per gram for spherical sand and anthracite media with diameters of 1 mm. This shows the rough and porous nature that the surface coatings have in order to result in the measured surface areas. There was good agreement for surface areas of duplicate samples analyzed for Durham and Newport News anthracite media.

Figure 4-28 shows a linear correlation between surface area and Mn coating levels. There is good agreement between the correlation found in this study, and that found by Merkle et al (1997), also shown in Figure 4-28. The correlation indicates that metal coating level and surface area are directly proportional; the more metal coating found on a filter media, the more surface area it is likely to have.

There are two types of data plotted in Figure 4-28. Samples have been separated into two sets; first stage filter samples (closed symbols) and second stage filter samples (open symbols). First stage samples are taken from filters that practice particle and soluble metal removal in the same stage i.e., one filter stage with pre-filter chlorination. Second stage filter samples are defined as samples taken from a filter which is used primarily to remove soluble metals, and has another media filter, primarily for particle removal, upstream of it in the treatment process. Samples of this type include samples taken from the second stage filters of the Carno and Cantref WTW, as well as media from a post-filter manganese contactor.

The linear correlation in Figure 4-28 is only applied to the results from the first stage samples. The samples analyzed from second stage filters were found to have much less surface area per amount of Mn oxide coating than found for the first stage samples. No samples defined here as second stage samples were analyzed during the Merkle et al (1997) study. It is possible that lower surface area results for the second stage media are due to the lack of particle removal occurring the second stage. Merkle et al (1997) speculates in his report that there is a possibility that particles become encapsulated or cemented in an oxide coating if such a coating is continuously forming. These particles could contribute a significant amount to the irregularity and internal porosity of the oxide coating, thus contributing to the surface area of a media. Therefore, if such particles were not present and not able to become enmeshed in the coating, as in a second stage filter, a lower surface area may result.

4.2.4 Mn Uptake

The impact of metal coating level on Mn uptake by adsorption to media was studied as part of this report. Mn uptake by sampled media was measured during the characterization process. The standard protocol for measuring Mn uptake capacity described in Chapter 3 was used. The use of the standard protocol ensures that the only variable between laboratory Mn uptake experiments is the amount of available sites for adsorption present on the oxide coated filter media.

A set of results of characterizing Mn uptake capacity are shown in Figure 4-29. This plot shows the Mn uptake of each sub-sample taken from a core of filter media versus media depth; Mn coating level versus depth is also shown. The oxide coating level decreases with depth, and the Mn uptake varies in the same manner. The top levels of the filter media core (Harwood's Mill) had the highest amounts of Mn uptake, while the lower layers of the filter had much less Mn uptake. The Mn uptake of the media was measured for two different conditions, as-is and regenerated, as noted in Figure 4-29. An explanation of these two media states is given in Section 4.2.4.2.

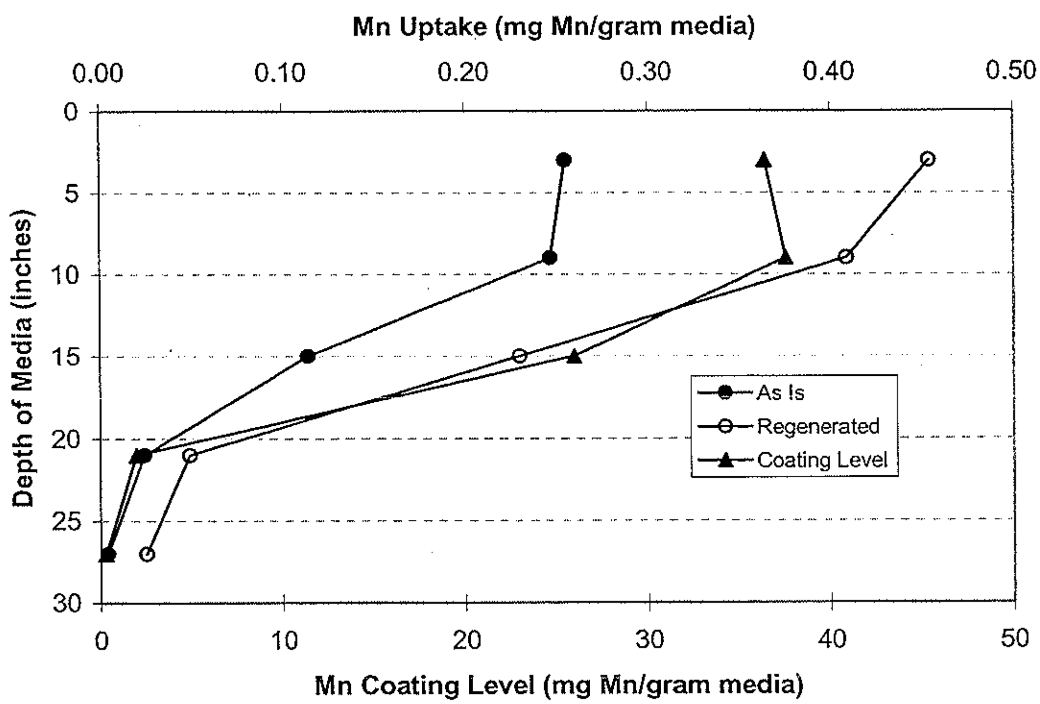

Figure 4-29 Mn Uptake Capacity and Mn Oxide Coating Level

4.2.4.1 Mn Uptake and Mn Coating Level

The results in Figure 4-29 suggest a relationship between Mn coating level and Mn uptake. Results from the single media core show that Mn uptake is directly proportional to the amount of Mn coating on the filter media. The more Mn coating a filter media has, the more soluble Mn it is able to adsorb. To better understand this relationship, results from many Mn coating and Mn uptake analyses (in the regenerated condition) were compared, as shown in Figure 4-30.

The results show that in general, Mn uptake increases with an increase in the amount of Mn coating on a filter media. For Mn coating levels less than approximately 15 mg Mn per gram of media, uptake appears to increase linearly with oxide coating. However, as the amount of Mn coating increases to higher levels, the Mn uptake increases much less. For Mn coating levels greater than 20 mg Mn per gram of media, a further increase in Mn coating does not correlate to a proportional increase in Mn uptake. This phenomenon is likely caused by the depth and porous nature of the metal oxide coating. Adsorption sites deep within small pores in the coating may not be accessible to aqueous Mn and chlorine and thus are not able to participate in the adsorption process in the time period of the experiments.

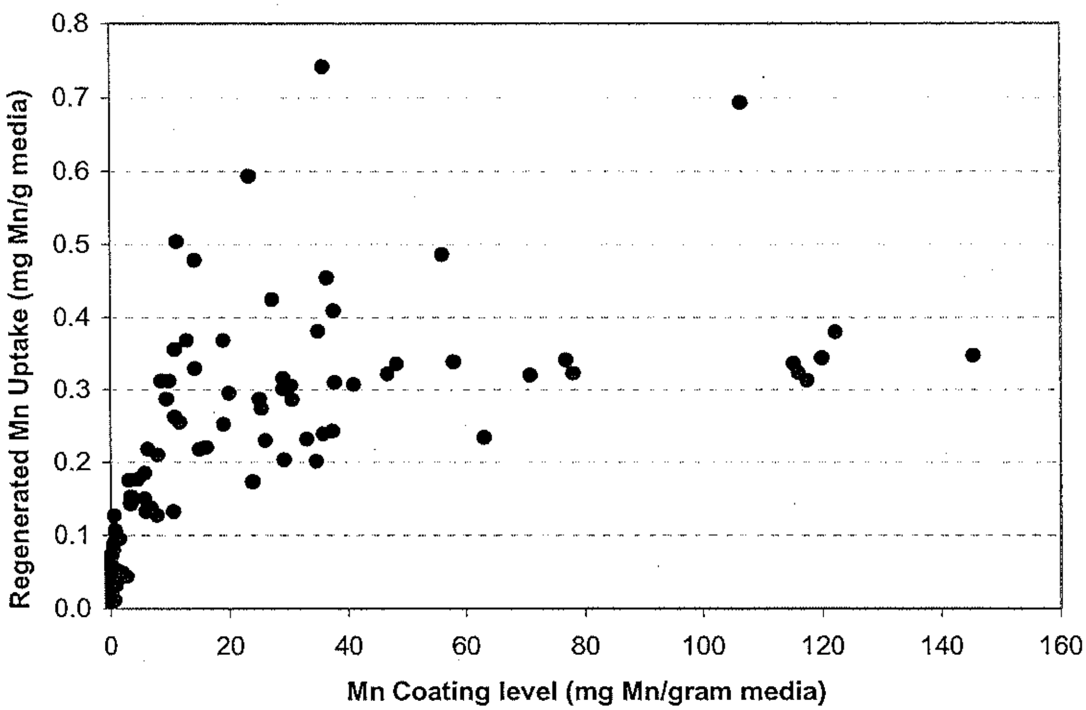

Figure 4-30 Mn Uptake vs. Mn Coating

4.2.4.2 Mn Adsorption Before and After Regeneration

Mn uptake of sampled filter media was measured before and after regeneration with free chlorine. In the tests conducted prior to regeneration, the media was in the same condition as it was when initially collected from the filter; this is referred to as the 'as-is' condition. After regeneration in a chlorine solution the media is said to be in the 'regenerated' state. Comparisons of Mn uptake for the as-is and regenerated conditions allow an analysis of the effectiveness of the pre-chlorination regime at a given WTP.

Figure 4-31 shows a correlation between the as-is and regenerated Mn uptake of numerous filter media samples. There are two types of data plotted in Figure 4-31; filter media that had been receiving chlorine and filter media that had not. As expected, the samples that were taken from filters that were not receiving pre-filter chlorine had very low Mn uptake in the as-is condition. However, once these samples were exposed to chlorine and regenerated, Mn uptake increased substantially. These points, noted by open circles, fall well above the linear correlation line for the results from samples that had been receiving pre-filter chlorine. The data indicate that even though the media had not been receiving pre-filter chlorine and the adsorption sites on the media were exhausted, upon the re-introduction of chlorine, the uptake capability returned. This result is also reflected in Figure 4-29, where the regenerated media had a higher measured Mn uptake than the media in the as-is condition. This increase in Mn uptake was found for each depth of sub-sample analyzed. In general, the regenerated Mn uptake of a Mn coated media was approximately 130% of the as-is Mn uptake.

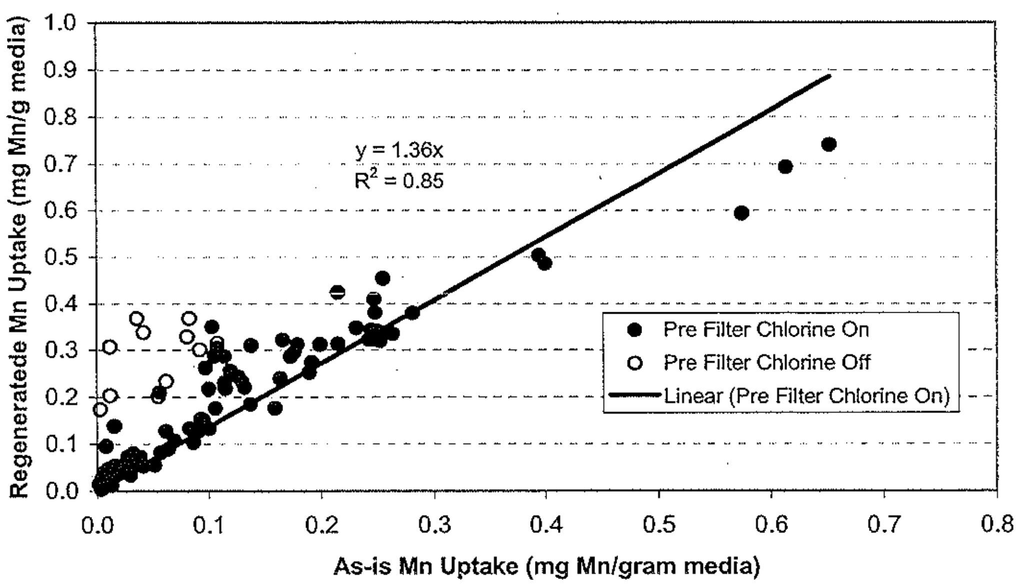

Figure 4-31 Mn Uptake Before and After Regeneration

4.2.5 Impact of Pre-Filter Chlorine on Mn Uptake

4.2.5.1 Lab Scale Study

The results in Figure 4-31 demonstrate the impact of laboratory batch chlorine regeneration on Mn adsorption. The Stamford WTP had ceased pre-filter chlorination during the winter months in an effort to reduce cost and disinfection by-product formation. Studies were conducted with Stamford media at the lab scale to determine if Mn uptake capability could be regenerated with pre-filter chlorine after several months of operation with no pre-filter chlorination. A sample of Stamford media collected in March, 2005 was exposed to a feed Mn solution (0.1 mg/L Mn) until uptake had ceased and the media was saturated. Then, a dose of chlorine (2.0 mg/L Cl_2) was added to the influent to the media. The results for chlorine residual and Mn concentration are shown in Figure 4-32.

Prior to the start of the pre-filter chlorination, the column influent and effluent Mn concentrations were the same, indicating that the media was saturated. Almost immediately after initiation of chlorination the effluent Mn concentration began to drecrease precipitously. After approximately 250 minutes, the effluent Mn concentration decreased from 0.1 mg/L to less than 0.01 mg/L. After a period of time, chlorine began to appear in the effluent of the column and steadily increased, indicating that the media surface sites had been regenerated. Approximately 500 minutes after the initiation of the chlorine dose, the effluent Mn and Cl_2 concentrations had reached equilibrium. The difference between the influent and effluent Cl_2 concentrations (0.4 mg/L) was similar to the predicted stoichiometric chlorine demand for Mn oxidation (~0.8 mg/L). After equilibrium was established, the influent chlorine dose was turned off. Soon after, the effluent Mn concentration began to increase.

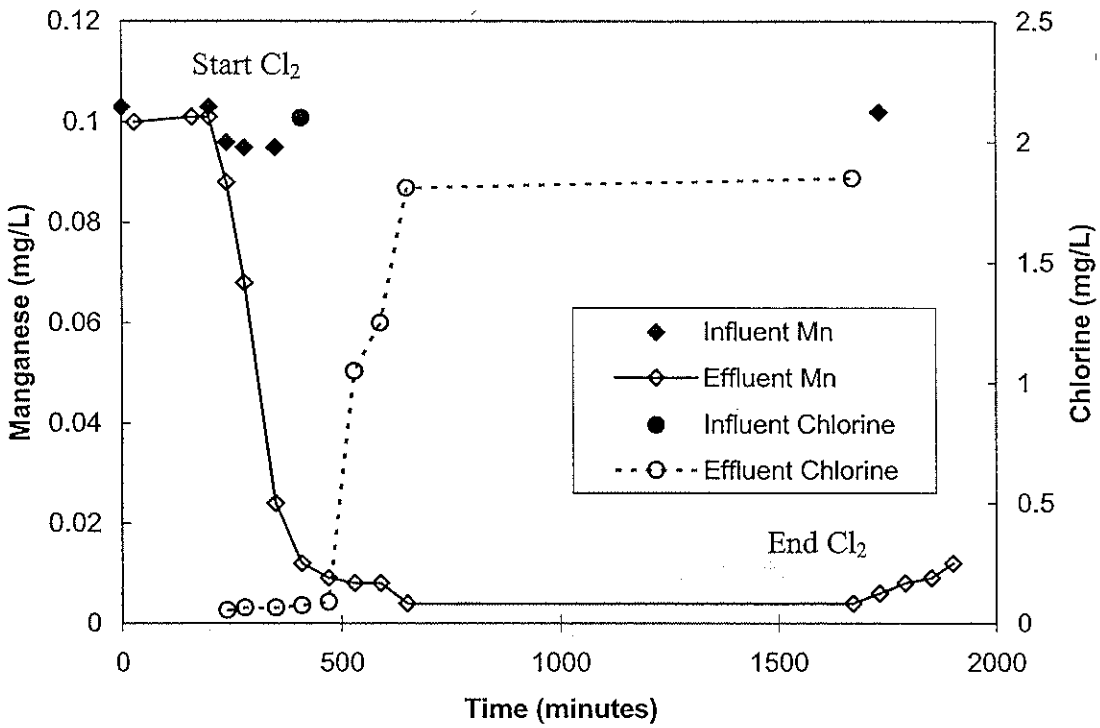

Figure 4-32 In-Line Regeneration of Stamford Media (pH = 6.3, Hydraulic Loading Rate = 10 gpm/ft^2)

4.2.5.2 Full Scale Study

The laboratory study demonstrated successful resumption of Mn uptake following a restart of pre-filter chlorine for the Stamford media. At the full scale, the Stamford WTP resumed pre-filter chlorination on May 25, 2005 in preparation for the expected seasonal increase in raw water Mn concentrations.

Figure 4-33 shows the influent and effluent Cl_2 concentrations for the first stage filters from May 25, 2005 to May 31, 2005. The Cl_2 dose to the filter was approximately 2.0

mg/L. After almost 24 hours, Cl_2 began to gradually appear in the effluent of the filter and appeared to stabilized at about 0.6 mg/L.

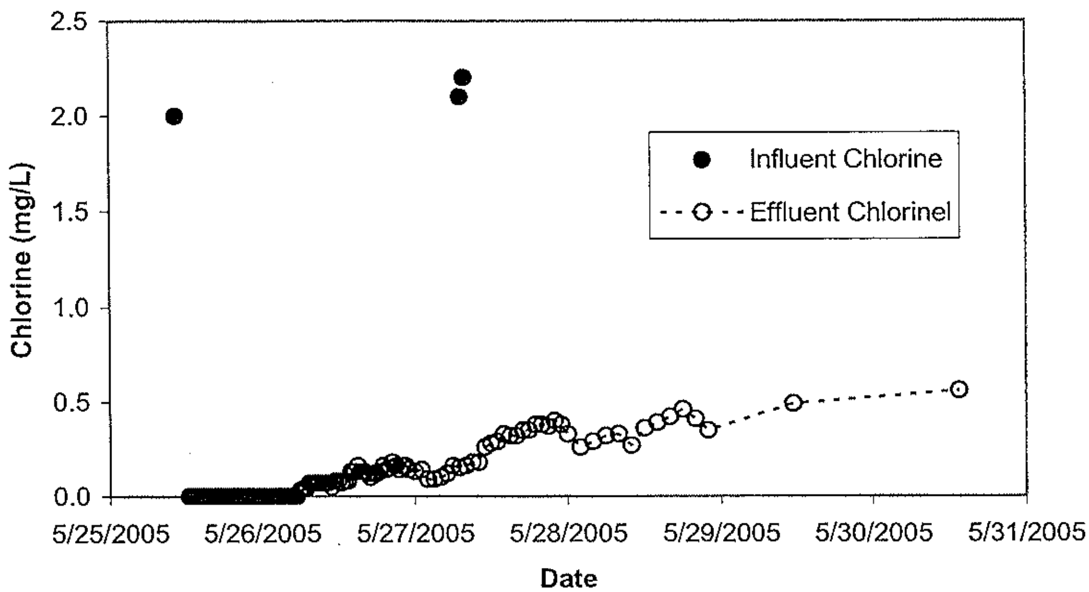

Figure 4-33 Full Scale Chlorination of Stamford 1st Stage Sand Filter

Figure 4-34 shows raw water and combined filter effluent (CFE) Mn concentration for the Stamford WTP from April 14, 2005 to September 19, 2005. On the day that pre-filter chlorination was started, the Mn concentration in the effluent changed very little. However, within days, the filter effluent Mn concentration had decreased and remained constant at approximately 0.005 mg/L. Soon after this period, the raw water Mn began to increase, rising to a maximum value of over 0.6 mg/L. During this time, the filters at Stamford provided excellent levels of Mn removal despite having not receiving chlorine during the winter and spring months. The resumption of Mn uptake after months without pre-filter chlorination illustrates the robust nature of the Mn uptake process and the ability of WTPs to optimize pre-filter chlorination based on Mn removal needs and concerns with DBPs. Other measurements during 2005 showed that the Mn coating level did not decrease during the January to May period without pre-filter chlorine.

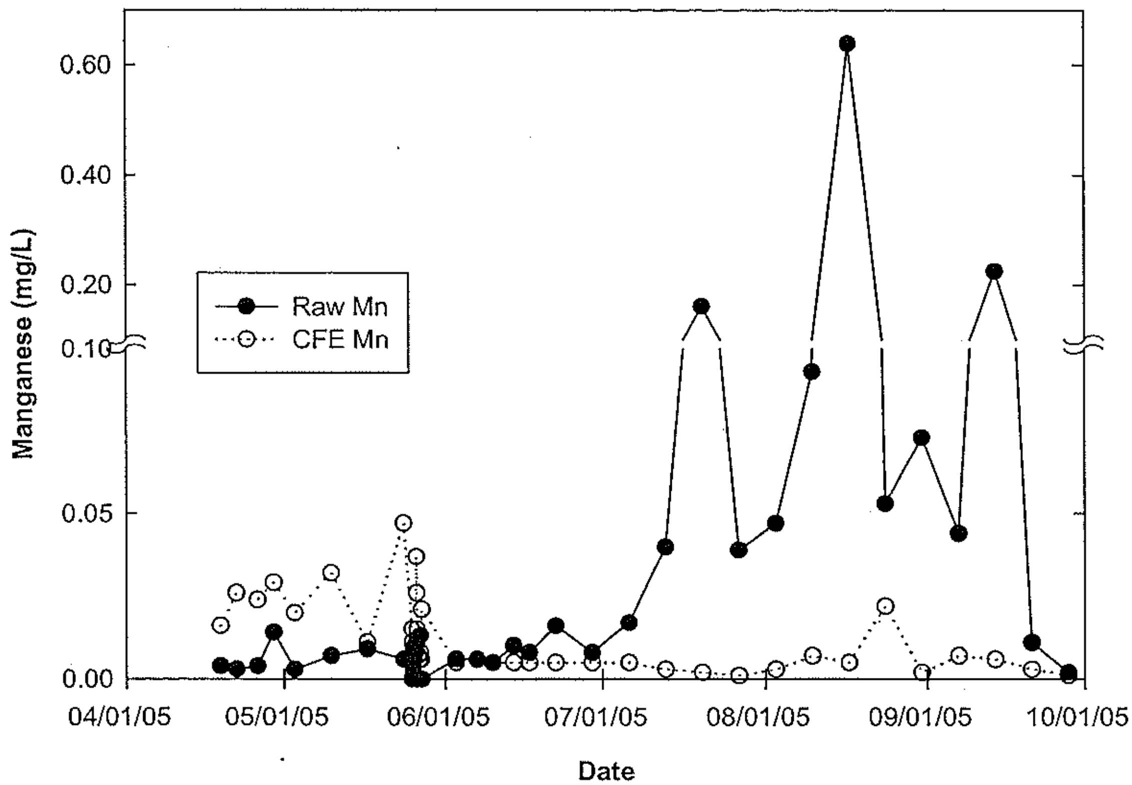

Figure 4-34 Full Scale Mn Removal at Stamford WTP

5.0 Summary, Conclusions and Recommendations

5.1 *Summary*

The objectives of this research were to characterize filter media used for Mn removal by adsorption of Mn to oxide coatings on the media. Samples were collected at nine surface water treatment plants. Size, oxide coating level, surface area and Mn uptake capacity of the media were measured in the characterization process. The impact of changes in pre-filter chlorination on Mn uptake were also studied at the laboratory and full scale.

5.2 *Conclusions*

The results of this research lead to the following conclusions:

- The surface coating on filter media consists of several metals including Mn, Fe and Al. The relative metals ratios are very consistent despite changes in the overall amount of metal coating on a media.

- Mn coating levels were found to range from less than 0.5 mg to over 120 Mn per gram of media in the upper levels of a filter. In general, the lower depths of a filter had significantly less Mn coating than the top. The Mn oxide coating level was also found to be independent of media type. There was a significant amount of statistical variability in the coating level results. For Mn levels greater than 1 mg Mn per gram of media the variability of coating level between to samples taken from the same sub-sample was approximately 22% while between core variability was 33% on average.

- The measured BET surface area of a media is directly proportional to the amount of Mn coating on the media. This is attributed to the irregularity and porosity of the oxide coating. This result only applies to samples taken from filters which remove particulate matter and soluble metals in the same filtration step. It is possible that a significant amount of this surface area is caused by the encapsulation of particulate matter in the oxide coating. Samples with Mn oxide coating levels ranging from approximately 0.1 to 100 mg Mn per gram of media had measured surface areas ranging from 1.9 to 92 m^2 per gram of media.

- Mn uptake increases with an increase in Mn oxide coating on a filter media. However, at coating levels of above 20 mg Mn per gram of media, a further increase in coating level did not necessarily equate to an increase in Mn uptake. The average uptake for a media with approximately 20 mg Mn per gram of media coating was found to be approximately 0.30 mg Mn per gram of media. The average uptake capacity for a media with approximately 40 mg Mn per gram of media was found to be approximately 0.33 mg Mn per gram of media. The lack of Mn uptake increase with a doubling of Mn coating level was attributed to the rough, porous nature of the oxide coating, making some sites deep within the coating not available for soluble Mn uptake.

- The Mn uptake capability of filter media in the as-is condition is approximately 70% of the Mn uptake for the same media after being regenerated overnight with a 20 mg/L chlorine solution.

- In a case study, stopping pre-filter chlorination for several months during periods of low raw water Mn did not adversely affect Mn uptake capability after pre-filter chlorination was resumed. No measurable amount of metal oxide coating was lost during this period. The Stamford WTP had stopped pre-chlorinating its filters for approximately 5 months in the winter and spring months. Upon resumption of pre-filter chlorination at the lab scale, Mn uptake resumed almost immediately.

5.3 Recommendations

Based on the above conclusions it is recommended that for WTPs practicing soluble Mn adsorption/oxidation a full understanding of the characteristics of the filter media should be obtained. Many aspects of the Mn oxide coated filter media can affect the adsorption process. For example, an understanding of the as-is versus regenerated Mn uptake capability of a plant's filter media would allow an assessment of the effectiveness of a pre-filter chlorine dose.

The media coating has been shown to contain significant amounts of iron, aluminum and calcium. Therefore, filtration with oxide coated media may be effective at removal of other soluble metals in a WTP. Based on surface area results, it is also possible that a significant amount of particulate matter is encapsulated in the oxide coating.

Mn adsorption with oxide coated media has been shown to be a robust process. Even after months of not receiving pre-filter chlorine, Mn adsorption was shown to resume if pre-filter chlorine was restarted at the lab and full scale. This nature of the process may allow WTPs to optimize their pre-filter chlorine regime with respect to soluble metal removal. A savings in cost and DBP formation may be obtained if pre-filter chlorination is practiced only when needed based on raw water Mn levels.

Further research is recommended to investigate some of the unexpected results regarding the relationship between surface area and Mn oxide coating levels. It is possible that particles encapsulated in the oxide coating contribute a significant amount of surface area to the filter media. Additional research is also recommended to investigate the mechanisms responsible for the consistency in the ratios of metals in the media coating.

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Appendix A: Metals Extraction Data

Table A-1 Trap Falls Metal Extraction Data

Date	Top depth (in)	Botton Depth (in)	Core	Average Depth (in)	Fluid Amount (L)	Dilution	ICP [Mn2+] (mg/L)	Mn2+ coating (mg/g)	ICP [Fe] (mg/L)	Fe coating (mg/g)	ICP [Al] (mg/L)	Al coating (mg/g)
16-Aug-05	0	5	A	2.5	0.25	25	13.53	56.38	0.541	2.25	7.57	31.54
16-Aug-05	0	5	A	2.5	0.25	25	10.46	56.75	0.425	2.31	5.705	30.95
16-Aug-05	5	13	A	9	0.25	25	10.87	58.13	0.416	2.22	5.93	31.71
16-Aug-05	5	13	A	9	0.25	25	10.69	57.18	0.438	2.34	5.898	31.55
16-Aug-05	13	20	A	16.5	0.25	25	4.273	16.64	0.207	0.81	2.403	9.36
16-Aug-05	13	20	A	16.5	0.25	25	3.875	15.65	0.214	0.86	2.178	8.80
16-Aug-05	20	24	A	22	0.25	25	0.191	0.68	0.043	0.15	0.202	0.71
16-Aug-05	20	24	A	22	0.25	25	0.185	0.67	0.033	0.12	0.203	0.74
16-Aug-05	24	29	A	26.5	0.25	25	0.089	0.30	0.025	0.08	0.144	0.49
16-Aug-05	24	29	A	26.5	0.25	25	0.051	0.20	0.023	0.09	0.11	0.44
16-Aug-05	0	6	B	3	0.25	25	8.439	41.47	0.377	1.85	4.742	23.30
16-Aug-05	0	6	B	3	0.25	25	7.937	40.05	0.375	1.89	4.461	22.51
16-Aug-05	6	12	B	9	0.25	25	7.376	39.17	0.341	1.81	4.179	22.19
16-Aug-05	6	12	B	9	0.25	25	8.223	39.59	0.379	1.82	4.652	22.40
16-Aug-05	12	18	B	15	0.25	25	7.51	34.81	0.358	1.66	4.228	19.60
16-Aug-05	12	18	B	15	0.25	25	8.16	32.66	0.376	1.50	4.576	18.31
16-Aug-05	18	22	B	20	0.25	25	0.27	1.00	0.043	0.16	0.27	1.00
16-Aug-05	18	22	B	20	0.25	25	0.093	0.34	0.01	0.04	0.107	0.39
16-Aug-05	22	28	B	25	0.25	25	0.185	0.58	0.037	0.12	0.275	0.86
16-Aug-05	22	28	B	25	0.25	25	0.066	0.24	0.022	0.08	0.153	0.56
16-Aug-05	0	6	C	3	0.25	25	8.531	36.49	0.394	1.69	4.861	20.79
16-Aug-05	0	6	C	3	0.25	25	8.704	36.37	0.431	1.80	4.989	20.85
16-Aug-05	6	12	C	9	0.25	25	7.976	37.79	0.364	1.72	4.454	21.10
16-Aug-05	6	12	C	9	0.25	25	7.12	37.35	0.315	1.65	3.968	20.82
16-Aug-05	12	18	C	15	0.25	25	5.517	24.94	0.273	1.23	3.155	14.26
16-Aug-05	12	18	C	15	0.25	25	5.755	27.03	0.288	1.35	3.266	15.34
16-Aug-05	18	24	C	21	0.25	25	0.443	1.56	0.059	0.21	0.368	1.30
16-Aug-05	18	24	C	21	0.25	25	0.57	2.35	0.051	0.21	0.415	1.71
16-Aug-05	24	29	C	26.5	0.25	25	0.088	0.35	0.042	0.16	0.169	0.66
16-Aug-05	24	29	C	26.5	0.25	25	0.063	0.22	0.036	0.13	0.16	0.57
16-Aug-05	0	6	D	3	0.25	25	6.457	33.00	0.335	1.71	3.719	19.00
16-Aug-05	0	6	D	3	0.25	25	0	0.00	0	0.00	0	0.00
16-Aug-05	6	12	D	9	0.25	25	6.693	33.45	0.316	1.58	3.804	19.01
16-Aug-05	6	12	D	9	0.25	25	6.359	33.36	0.306	1.61	3.625	19.02
16-Aug-05	12	18	D	15	0.25	25	3.596	15.88	0.21	0.93	2.121	9.37
16-Aug-05	12	18	D	15	0.25	25	3.465	17.36	0.183	0.92	2.001	10.03
16-Aug-05	18	22	D	20	0.25	25	0.319	1.27	0.049	0.19	0.28	1.11
16-Aug-05	18	22	D	20	0.25	25	0.134	0.67	0.035	0.17	0.175	0.87
16-Aug-05	22	25	D	23.5	0.25	25	0.214	0.82	0.04	0.15	0.236	0.90
16-Aug-05	22	25	D	23.5	0.25	25	0.317	1.21	0.051	0.19	0.307	1.17
16-Aug-05	0	6	E	3	0.25	25	6.863	34.35	0.333	1.67	3.888	19.46
16-Aug-05	0	6	E	3	0.25	25	7.888	34.79	0.387	1.71	4.455	19.65
16-Aug-05	6	12	E	9	0.25	25	7.134	32.76	0.377	1.73	4.102	18.83
16-Aug-05	6	12	E	9	0.25	25	6.481	32.00	0.341	1.68	3.671	18.12
16-Aug-05	12	16	E	14	0.25	25	3.075	14.49	0.211	0.99	1.813	8.54
16-Aug-05	12	16	E	14	0.25	25	2.65	10.45	0.151	0.60	1.585	6.25
16-Aug-05	16	20	E	18	0.25	25	0.144	0.54	0.035	0.13	0.176	0.66
16-Aug-05	16	20	E	18	0.25	25	0.118	0.44	0.023	0.09	0.14	0.53
16-Aug-05	20	24	E	22	0.25	25	0.048	0.18	0.036	0.14	0.129	0.48
16-Aug-05	20	24	E	22	0.25	25	0.055	0.24	0.025	0.11	0.134	0.57
16-Aug-05	0	6	F	3	0.25	25	8.021	41.37	0.373	1.92	4.494	23.18
16-Aug-05	0	6	F	3	0.25	25	6.343	32.78	0.264	1.36	3.483	18.00
16-Aug-05	6	12	F	9	0.25	25	7.706	42.26	0.374	2.05	4.327	23.73
16-Aug-05	6	12	F	9	0.25	25	8.781	44.34	0.42	2.12	4.824	24.36
16-Aug-05	12	18	F	15	0.25	25	7.725	37.59	0.361	1.76	4.382	21.32
16-Aug-05	12	18	F	15	0.25	25	7.164	34.91	0.327	1.59	4.011	19.54
16-Aug-05	18	24	F	21	0.25	25	1.052	3.81	0.083	0.30	0.68	2.46
16-Aug-05	18	24	F	21	0.25	25	0.717	3.17	0.077	0.34	0.508	2.24
16-Aug-05	24	30	F	27	0.25	25	0.259	0.96	0.019	0.07	0.142	0.53
16-Aug-05	24	30	F	27	0.25	25	0.465	1.73	0.05	0.19	0.351	1.31

Table A-2 Warner Metals Extraction Data

Date	Top depth (in)	Botton Depth (in)	Core	Average Depth (in)	Fluid Amount (L)	Dilution	ICP [Mn2+] (mg/L)	Mn2+ coating (mg/g)	ICP [Fe] (mg/L)	Fe coating (mg/g)	ICP [Al] (mg/L)	Al coating (mg/g)
17-Aug-05	0	5	7C	2.5	0.25	1	61.21	10.55	7.32	1.26	60.27	10.39
17-Aug-05	0	5	7C	2.5	0.25	1	61.29	11.01	7.788	1.40	59.99	10.78
17-Aug-05	5	10	7C	7.5	0.25	1	50.04	9.95	6.883	1.37	48.53	9.65
17-Aug-05	5	10	7C	7.5	0.25	1	52.03	8.97	7.302	1.26	52.07	8.97
17-Aug-05	10	15	7C	12.5	0.25	1	39.75	6.13	7.509	1.16	41.42	6.39
17-Aug-05	10	15	7C	12.5	0.25	1	39.7	6.28	7.194	1.14	41.02	6.49
17-Aug-05	15	20	7C	17.5	0.25	1	20.83	3.74	5.448	0.98	23.4	4.20
17-Aug-05	15	20	7C	17.5	0.25	1	20.16	3.50	6.393	1.11	23.42	4.07
17-Aug-05	20	25	7C	22.5	0.25	1	1.067	0.15	1.736	0.24	7.308	1.02
17-Aug-05	20	25	7C	22.5	0.25	1	0.931	0.15	1.706	0.28	6.234	1.01
17-Aug-05	0	7	9C	3.5	0.25	1	72.4	14.06	8.187	1.59	70.89	13.77
17-Aug-05	0	7	9C	3.5	0.25	1	70.27	14.42	7.9	1.62	68.54	14.06
17-Aug-05	7	14	9C	10.5	0.25	1	67.97	12.47	7.755	1.42	63.71	11.69
17-Aug-05	7	14	9C	10.5	0.25	1	72.58	13.06	8.422	1.52	71.79	12.92
17-Aug-05	14	21	9C	17.5	0.25	1	40.95	7.25	8.966	1.59	41.24	7.30
17-Aug-05	14	21	9C	17.5	0.25	1	34.48	6.17	9.991	1.79	35.34	6.32
17-Aug-05	21	24	9C	22.5	0.25	1	1.178	0.16	1.182	0.16	7.35	1.00
17-Aug-05	21	24	9C	22.5	0.25	1	1.063	0.17	1.585	0.25	6.493	1.01
17-Aug-05	24	30	9C	27	0.25	1	1.785	0.32	1.659	0.29	6.168	1.09
17-Aug-05	24	30	9C	27	0.25	1	1.381	0.23	3.288	0.56	6.467	1.10

Date	Top depth (in)	Botton Depth (in)	Core	Average Depth (in)	Fluid Amount (L)	Dilution	ICP [Mn2+] (mg/L)	Mn2+ coating (mg/g)	ICP [Fe] (mg/L)	Fe coating (mg/g)	ICP [Al] (mg/L)	Al coating (mg/g)	ICP [Ca] (mg/L)	Ca coating (mg/g)
10-Jan-06	0	5	7B	2.5	0.25	1	37.86	8.70	5.14	1.18	38.53	8.86	3.33	0.77
10-Jan-06	0	5	7B	2.5	0.25	1	39.50	7.90	4.99	1.00	41.11	8.22	3.76	0.75
10-Jan-06	5	10	7B	7.5	0.25	1	36.95	8.10	4.98	1.09	38.81	8.51	3.72	0.82
10-Jan-06	5	10	7B	7.5	0.25	1	35.84	8.17	4.69	1.07	36.96	8.43	3.53	0.80
10-Jan-06	10	15	7B	12.5	0.25	1	31.55	7.58	4.90	1.18	33.19	7.98	3.49	0.84
10-Jan-06	10	15	7B	12.5	0.25	1	37.80	8.86	4.82	1.13	38.81	9.10	3.36	0.79
10-Jan-06	15	20	7B	17.5	0.25	1	40.34	8.86	6.13	1.34	42.10	9.24	4.36	0.96
10-Jan-06	15	20	7B	17.5	0.25	1	15.18	3.14	3.06	0.63	18.32	3.79	2.51	0.52
10-Jan-06	20	27	7B	23.5	0.25	1	0.75	0.11	0.78	0.11	7.06	1.00	0.33	0.05
10-Jan-06	20	27	7B	23.5	0.25	1	0.77	0.15	0.82	0.16	5.54	1.06	0.36	0.07
10-Jan-06	0	5	9A	2.5	0.25	1	58.29	14.87	6.10	1.55	60.50	15.43	3.01	0.77
10-Jan-06	0	5	9A	2.5	0.25	1	65.90	15.42	6.69	1.57	69.93	16.36	3.14	0.74
10-Jan-06	5	10	9A	7.5	0.25	1	74.57	15.75	8.09	1.71	79.11	16.71	4.40	0.93
10-Jan-06	5	10	9A	7.5	0.25	1	67.18	16.15	7.60	1.83	70.82	17.02	4.52	1.09
10-Jan-06	10	15	9A	12.5	0.25	1	79.85	16.72	8.49	1.78	85.86	17.97	4.30	0.90
10-Jan-06	10	15	9A	12.5	0.25	1	71.77	15.45	7.16	1.54	74.80	16.10	4.09	0.88
10-Jan-06	15	20	9A	17.5	0.25	1	71.83	17.53	7.28	1.78	74.03	18.07	4.19	1.02
10-Jan-06	15	20	9A	17.5	0.25	1	76.14	17.58	7.84	1.81	80.82	18.66	4.41	1.02
10-Jan-06	20	27	9A	23.5	0.25	1	11.00	2.40	3.15	0.69	14.80	3.23	1.57	0.34
10-Jan-06	20	27	9A	23.5	0.25	1	14.70	2.64	2.99	0.54	18.19	3.27	1.54	0.28

Table A-3 Stamford Metals Extraction Data

Date	Top depth (in)	Botton Depth (in)	Core	Average Depth (in)	Fluid Amount (L)	Dilution	ICP [Mn2+] (mg/L)	Mn2+ coating (mg/g)	ICP [Fe] (mg/L)	Fe coating (mg/g)	ICP [Al] (mg/L)	Al coating (mg/g)
23-Aug-05	0	6	A	3	0.25	25	6.011	25.39	0.573	2.42	6.498	27.45
23-Aug-05	0	6	A	3	0.25	25	6.899	28.83	0.674	2.82	7.514	31.40
23-Aug-05	0	6	B	3	0.25	25	7.610	29.91	0.688	2.70	7.774	30.55
23-Aug-05	0	6	B	3	0.25	25	7.000	31.02	0.619	2.74	7.027	31.14
23-Aug-05	0	6	C	3	0.25	1	0.005	0.001	0.020	0.004	0.216	0.038
23-Aug-05	0	6	C	3	0.25	1	0.004	0.001	0.022	0.004	0.491	0.081
23-Aug-05	0	6	D	3	0.25	1	0.004	0.001	0.021	0.003	0.261	0.043
23-Aug-05	0	6	D	3	0.25	1	0.002	0.000	0.021	0.003	0.252	0.039

Table A-4a Brown Metals Extraction Data

Date	Top depth (in)	Botton Depth (in)	Core	Average Depth (in)	Fluid Amount (L)	Dilution	ICP [Mn2+] (mg/L)	Mn2+ coating (mg/g)	ICP [Fe] (mg/L)	Fe coating (mg/g)	ICP [Al] (mg/L)	Al coating (mg/g)
2-Jun-05	0	6	A	3	0.25	25	16.2	110.75	1.301	8.89	4.054	27.72
2-Jun-05	0	6	A	3	0.25	25	14.4	101.89	1.091	7.72	2.006	14.19
2-Jun-05	6	12	A	9	0.25	25	10.77	57.05	0.707	3.75	4.214	22.32
2-Jun-05	6	12	A	9	0.25	25	9.82	55.19	0.341	1.92	1.138	6.40
2-Jun-05	12	18	A	15	0.25	25	0.846	4.04	0.073	0.35	0.14	0.67
2-Jun-05	12	18	A	15	0.25	25	1.033	4.88	0.12	0.57	0.346	1.64
2-Jun-05	18	24	A	21	0.25	25	0.127	0.53	0.075	0.31	0.053	0.22
2-Jun-05	18	24	A	21	0.25	25	0.058	0.27	0.02	0.09	0.016	0.08
2-Jun-05	24	30	A	27	0.25	25	0.434	2.03	0.057	0.27	0.108	0.50
2-Jun-05	24	30	A	27	0.25	25	0.003	0.01	0	0.00	0.002	0.01
2-Jun-05	0	6	B	3	0.25	25	8.617	54.12	0.521	3.27	1.542	9.68
2-Jun-05	0	6	B	3	0.25	25	8.62	57.10	0.539	3.57	1.936	12.82
2-Jun-05	6	12	B	9	0.25	25	7.415	37.24	0.41	2.06	2.636	13.24
2-Jun-05	6	12	B	9	0.25	25	7.954	38.39	0.458	2.21	2.838	13.70
2-Jun-05	12	18	B	15	0.25	25	1.794	8.43	0.136	0.64	0.467	2.20
2-Jun-05	12	18	B	15	0.25	25	1.217	5.81	0.099	0.47	0.31	1.48
2-Jun-05	18	24	B	21	0.25	25	0.264	1.22	0.033	0.15	0.05	0.23
2-Jun-05	18	24	B	21	0.25	25	0.148	0.70	0.022	0.10	0.039	0.19
2-Jun-05	24	30	B	27	0.25	25	0.071	0.32	0.029	0.13	0.022	0.10
2-Jun-05	24	30	B	27	0.25	25	0.035	0.15	0.021	0.09	0.012	0.05
2-Jun-05	0	6	C	3	0.25	25	1.393	6.89	0.149	0.74	0.247	1.22
2-Jun-05	0	6	C	3	0.25	25	1.061	5.65	0.101	0.54	0.117	0.62
2-Jun-05	6	12	C	9	0.25	25	0.288	1.30	0.027	0.12	0.038	0.17
2-Jun-05	6	12	C	9	0.25	25	1.04	5.04	0.13	0.63	0.239	1.16
2-Jun-05	12	18	C	15	0.25	25	0.879	4.08	0.126	0.58	0.267	1.24
2-Jun-05	12	18	C	15	0.25	25	0.594	2.79	0.07	0.33	0.123	0.58
2-Jun-05	18	24	C	21	0.25	25	0.761	3.59	0.13	0.61	0.186	0.88
2-Jun-05	18	24	C	21	0.25	25	0.666	3.25	0.142	0.69	0.217	1.06
2-Jun-05	24	30	C	27	0.25	25	0.411	1.81	0.096	0.42	0.285	1.26
2-Jun-05	24	30	C	27	0.25	25	0.277	1.21	0.064	0.28	0.161	0.70
2-Jun-05	0	6	D	3	0.25	25	0.847	4.61	0.193	1.05	0.11	0.60
2-Jun-05	0	6	D	3	0.25	25	0.831	4.64	0.101	0.56	0.074	0.41
2-Jun-05	6	12	D	9	0.25	25	0.951	4.91	0.12	0.62	0.107	0.55
2-Jun-05	6	12	D	9	0.25	25	0.4	2.19	0.042	0.23	0.041	0.22
2-Jun-05	12	18	D	15	0.25	25	0.74	3.93	0.106	0.56	0.062	0.33
2-Jun-05	12	18	D	15	0.25	25	0.799	4.34	0.111	0.60	0.097	0.53
2-Jun-05	18	24	D	21	0.25	25	0.609	3.00	0.11	0.54	0.1	0.49
2-Jun-05	18	24	D	21	0.25	25	0.521	2.56	0.079	0.39	0.078	0.38
2-Jun-05	24	30	D	27	0.25	25	0.199	0.90	0.029	0.13	0.064	0.29
2-Jun-05	24	30	D	27	0.25	25	0.22	1.03	0.035	0.16	0.082	0.38
2-Jun-05	0	6	E	3	0.25	25	3.688	21.42	0.698	4.05	0.168	0.98
2-Jun-05	0	6	E	3	0.25	25	4.102	25.30	0.59	3.64	0.161	0.99
2-Jun-05	6	12	E	9	0.25	25	5.387	34.09	0.814	5.15	0.227	1.44
2-Jun-05	6	12	E	9	0.25	25	5.463	37.62	0.678	4.67	0.189	1.30
2-Jun-05	12	18	E	15	0.25	25	2.536	12.67	1.105	5.52	0.119	0.59
2-Jun-05	12	18	E	15	0.25	25	1.728	9.66	0.41	2.29	0.06	0.34
2-Jun-05	18	24	E	21	0.25	25	0.247	1.16	0.143	0.67	0.013	0.06
2-Jun-05	18	24	E	21	0.25	25	0.134	0.63	0.091	0.43	0.007	0.03
2-Jun-05	24	30	E	27	0.25	25	0.063	0.27	0.173	0.75	0.0003	0.00
2-Jun-05	24	30	E	27	0.25	25	0.066	0.28	0.122	0.52	0.0001	0.00
2-Jun-05	0	6	F	3	0.25	25	5.433	31.68	0.855	4.99	0.21	1.22
2-Jun-05	0	6	F	3	0.25	25	5.868	32.06	0.944	5.16	0.209	1.14
2-Jun-05	6	12	F	9	0.25	25	4.573	27.84	0.88	5.36	0.177	1.08
2-Jun-05	6	12	F	9	0.25	25	4.471	26.92	0.825	4.97	0.154	0.93
2-Jun-05	12	18	F	15	0.25	25	3.178	18.18	0.61	3.49	0.091	0.52
2-Jun-05	12	18	F	15	0.25	25	3.494	19.18	0.935	5.13	0.15	0.82
2-Jun-05	18	24	F	21	0.25	25	0.734	3.42	0.198	0.92	0.02	0.09
2-Jun-05	18	24	F	21	0.25	25	0.925	4.27	0.264	1.22	0.027	0.12
2-Jun-05	24	30	F	27	0.25	25	0.23	1.03	0.183	0.82	0.013	0.06
2-Jun-05	24	30	F	27	0.25	25	0.269	1.15	0.252	1.08	0.017	0.07

Table A-4b Brown Metals Extraction Data

Date	Top depth (in)	Botton Depth (in)	Core	Average Depth (in)	Fluid Amount (L)	Dilution	ICP [Mn2+] (mg/L)	Mn2+ coating (mg/g)	ICP [Fe] (mg/L)	Fe coating (mg/g)	ICP [Al] (mg/L)	Al coating (mg/g)
29-Nov-05	0	6	3A	3	0.25	25	1.589	8.41	0.151	0.80	0.19	1.01
29-Nov-05	0	6	3A	3	0.25	25	1.376	6.71	0.141	0.69	0.195	0.95
29-Nov-05	6	12	3A	9	0.25	25	3.435	17.92	0.306	1.60	0.179	0.93
29-Nov-05	6	12	3A	9	0.25	25	3.706	19.04	0.311	1.60	0.251	1.29
29-Nov-05	12	18	3A	15	0.25	25	1.099	5.02	0.113	0.52	0.165	0.75
29-Nov-05	12	18	3A	15	0.25	25	1.298	5.72	0.146	0.64	0.197	0.87
29-Nov-05	18	24	3A	21	0.25	1	42.6	8.67	3.567	0.73	3.01	0.61
29-Nov-05	18	24	3A	21	0.25	1	30.65	5.28	3.669	0.63	5.571	0.96
29-Nov-05	24	30	3A	27	0.25	1	32.52	5.53	4.23	0.72	5.404	0.92
29-Nov-05	24	30	3A	27	0.25	1	75.21	19.78	6.814	1.79	3.957	1.04
29-Nov-05	0	6	3B	3	0.25	25	0.742	2.95	0.171	0.68	0.346	1.37
29-Nov-05	0	6	3B	3	0.25	25	0.721	3.06	0.137	0.58	0.331	1.40
29-Nov-05	6	12	3B	9	0.25	25	1.526	9.18	0.187	1.12	0.095	0.57
29-Nov-05	6	12	3B	9	0.25	25	1.777	9.74	0.215	1.18	0.165	0.90
29-Nov-05	12	18	3B	15	0.25	25	0.753	3.43	0.121	0.55	0.248	1.13
29-Nov-05	12	18	3B	15	0.25	25	1.092	4.72	0.187	0.81	0.352	1.52
29-Nov-05	18	24	3B	21	0.25	1	53.22	12.73	6.847	1.64	3.009	0.72
29-Nov-05	18	24	3B	21	0.25	1	56.74	13.61	6.861	1.65	4.172	1.00
29-Nov-05	24	30	3B	27	0.25	1	44.8	8.81	6.359	1.25	5.932	1.17
29-Nov-05	24	30	3B	27	0.25	1	39.82	8.66	5.861	1.27	6.686	1.45
29-Nov-05	0	6	5A	3	0.25	25	7.187	41.68	0.439	2.55	3.049	17.68
29-Nov-05	0	6	5A	3	0.25	25	7.238	41.41	0.468	2.68	3.089	17.67
29-Nov-05	6	12	5A	9	0.25	25	0.233	1.20	0.108	0.56	0.093	0.48
29-Nov-05	6	12	5A	9	0.25	25	0.241	1.01	0.08	0.34	0.112	0.47
29-Nov-05	12	18	5A	15	0.25	25	9.982	64.67	0.729	4.72	3.036	19.67
29-Nov-05	12	18	5A	15	0.25	25	11.01	67.56	0.787	4.83	3.338	20.48
29-Nov-05	18	24	5A	21	0.25	1	1.738	0.27	2.958	0.46	2.012	0.31
29-Nov-05	18	24	5A	21	0.25	1	0.399	0.06	0.783	0.12	0.348	0.05
29-Nov-05	24	30	5A	27	0.25	1	0.392	0.07	0.303	0.06	0.208	0.04
29-Nov-05	24	30	5A	27	0.25	1	0.162	0.02	0.207	0.03	0.134	0.02
29-Nov-05	0	6	5B	3	0.25	25	1.79	7.20	0.223	0.90	0.779	3.13
29-Nov-05	0	6	5B	3	0.25	25	1.01	4.34	0.127	0.55	0.44	1.89
29-Nov-05	6	12	5B	9	0.25	25	0.479	2.25	0.081	0.38	0.171	0.80
29-Nov-05	6	12	5B	9	0.25	25	0.935	4.36	0.121	0.56	0.399	1.86
29-Nov-05	12	18	5B	15	0.25	25	6.349	20.13	0.429	1.36	2.37	7.51
29-Nov-05	12	18	5B	15	0.25	25	7.13	38.06	0.505	2.70	2.655	14.17
29-Nov-05	18	24	5B	21	0.25	25	7.257	44.28	0.433	2.64	3.197	19.51
29-Nov-05	18	24	5B	21	0.25	25	6.79	40.51	0.396	2.36	2.999	17.89
29-Nov-05	24	30	5B	27	0.25	25	7.052	46.92	0.451	3.00	2.723	18.12
29-Nov-05	24	30	5B	27	0.25	25	8.242	46.12	0.51	2.85	3.158	17.67
29-Nov-05	0	6	7A	3	0.25	25	2.677	15.54	0.588	3.41	0.144	0.84
29-Nov-05	0	6	7A	3	0.25	25	1.308	6.29	0.399	1.92	0.069	0.33
29-Nov-05	6	12	7A	9	0.25	25	0.233	1.24	0.243	1.30	0.014	0.07
29-Nov-05	6	12	7A	9	0.25	25	0.369	1.59	0.325	1.40	0.023	0.10
29-Nov-05	12	18	7A	15	0.25	1	14.15	2.59	7.623	1.39	0.813	0.15
29-Nov-05	12	18	7A	15	0.25	1	2.874	0.42	4.839	0.70	0.317	0.05
29-Nov-05	18	24	7A	21	0.25	1	2.032	0.38	6.507	1.22	0.601	0.11
29-Nov-05	18	24	7A	21	0.25	1	1.605	0.30	3.482	0.65	0.305	0.06
29-Nov-05	24	30	7A	27	0.25	1	1.11	0.18	5.012	0.82	0.443	0.07
29-Nov-05	24	30	7A	27	0.25	1	1.31	0.23	5.032	0.88	0.442	0.08
29-Nov-05	0	6	7B	3	0.25	25	1.203	5.76	0.563	2.70	0.037	0.18
29-Nov-05	0	6	7B	3	0.25	25	1.188	5.94	0.564	2.82	0.04	0.20
29-Nov-05	6	12	7B	9	0.25	25	1.299	7.35	0.457	2.59	0.041	0.23
29-Nov-05	6	12	7B	9	0.25	25	1.412	7.32	0.607	3.15	0.048	0.25
29-Nov-05	12	18	7B	15	0.25	1	43.44	7.98	16.58	3.04	1.297	0.24
29-Nov-05	12	18	7B	15	0.25	1	33.7	6.60	13.51	2.65	0.952	0.19
29-Nov-05	18	24	7B	21	0.25	1	64.3	12.82	22.46	4.48	2.317	0.46
29-Nov-05	18	24	7B	21	0.25	1	61.53	12.62	21.24	4.36	1.94	0.40
29-Nov-05	24	30	7B	27	0.25	1	6.526	1.19	5.878	1.07	0.472	0.09
29-Nov-05	24	30	7B	27	0.25	1	5.201	1.04	6.389	1.27	0.471	0.09

Table A-5a Newport News Metals Extraction Data

Date	Top depth (in)	Botton Depth (in)	Core	Average Depth (in)	Date	Dilution	ICP [Mn2+] (ug/L)	Mn2+ coating (mg/g)	ICP [Fe] (ug/L)	Fe coating (mg/g)	ICP [Al] (ug/L)	Al coating (mg/g)		
2-May-05	0	6	A	3	2-May-05	50	3210	36.47	137.1	1.56	2216	25.17		
2-May-05	0	6	A	3	2-May-05	50	3450	38.87	135.6	1.53	2695	30.36		
2-May-05	6	12	A	9	2-May-05	50	2182	24.96	94	1.08	1615	18.47		
2-May-05	6	12	A	9	2-May-05	50	2753	31.30	146.6	1.67	2133	24.25		
2-May-05	12	18	A	15	2-May-05	50	3239	33.42	126.1	1.30	2064	21.29		
2-May-05	12	18	A	15	2-May-05	50	2501	26.19	119.7	1.25	2088	21.87		
2-May-05	18	24	A	21	2-May-05	50	2680	31.94	144.9	1.73	2057	24.51		
2-May-05	18	24	A	21	2-May-05	50	2860	28.87	169.5	1.71	2281	23.03		
2-May-05	24	30	A	27	2-May-05	50	857	8.83	108.3	1.12	805	8.29		
2-May-05	24	30	A	27	2-May-05	50	1024	9.67	90.1	0.85	1033	9.76		
2-May-05	30	36	A	33	2-May-05	50	117.5	0.89	33.7	0.25	182.2	1.37		
2-May-05	30	36	A	33	2-May-05	50	56.9	0.46	22.2	0.18	125.3	1.02		
2-May-05	0	6	B	3	2-May-05	50	4769	50.62	189.2	2.01	3332	35.37		
2-May-05	0	6	B	3	2-May-05	50	4265	42.87	166.6	1.67	3054	30.70		
2-May-05	6	12	B	9	2-May-05	50	4035	40.00	145.2	1.44	2855	28.30		
2-May-05	6	12	B	9	2-May-05	50	3852	35.49	135.6	1.25	2599	23.95		
2-May-05	12	18	B	15	2-May-05	50	2738	29.62	136.6	1.48	1994	21.57		
2-May-05	12	18	B	15	2-May-05	50	2638	30.95	131.6	1.54	2017	23.67		
2-May-05	18	24	B	21	2-May-05	50	2356	25.50	138	1.49	1868	20.21		
2-May-05	18	24	B	21	2-May-05	50	2467	24.59	147.3	1.47	1939	19.33		
2-May-05	24	30	B	27	2-May-05	50	714	7.19	53.8	0.54	679	6.84		
2-May-05	24	30	B	27	2-May-05	50	636	6.38	59.2	0.59	581	5.82		
2-May-05	30	36	B	33	2-May-05	50	83.5	0.54	34.8	0.23	146.9	0.96		
2-May-05	30	36	B	33	2-May-05	50	85.7	0.53	36.9	0.23	196.5	1.22		

Date	Top depth (in)	Botton Depth (in)	Core	Average Depth (in)	Wt. of Pan (g)	Dilution	ICP [Mn2+] (mg/L)	Mn2+ coating (mg/g)	ICP [Fe] (mg/L)	Fe coating (mg/g)	ICP [Al] (ug/L)	Al coating (mg/g)	ICP [Ca] (ug/L)	Ca coating (mg/g)
1-Nov-05	0	6	A	3	1.0037	25	8.363	40.79	0.313	1.53	5.501	26.83	0.277	1.35
1-Nov-05	0	6	A	3	1.0008	25	9.347	40.85	0.308	1.35	5.62	24.56	0.27	1.18
1-Nov-05	6	12	A	9	0.9964	25	9.368	34.17	0.432	1.58	6.874	25.08	0.408	1.49
1-Nov-05	6	12	A	9	0.9910	25	11.1	40.21	0.444	1.61	7.716	27.95	0.487	1.76
1-Nov-05	12	18	A	15	0.9900	25	8.098	29.86	0.245	0.90	4.357	16.07	0.267	0.98
1-Nov-05	12	18	A	15	0.9948	25	9.708	32.79	0.436	1.47	7.067	23.87	0.436	1.47
1-Nov-05	18	24	A	21	0.9962	1	164.2	22.66	10.000	1.38	171.9	23.73	10.61	1.46
1-Nov-05	18	24	A	21	1.0014	1	149.6	22.74	9.103	1.38	150.8	22.92	8.966	1.36
1-Nov-05	24	30	A	27	0.9989	1	74.95	10.16	4.493	0.61	59.13	8.01	7.297	0.99
1-Nov-05	24	30	A	27	0.9948	1	107.8	14.35	6.473	0.86	95.48	12.71	8.773	1.17
1-Nov-05	30	36	A	33	0.9986	1	6.047	0.79	1.052	0.14	7.084	0.93	1.517	0.20
1-Nov-05	30	36	A	33	1.0010	1	8.893	1.16	2.226	0.29	11.76	1.53	3.479	0.45
1-Nov-05	0	6	B	3	1.0060	25	10.37	40.89	0.431	1.70	7.574	29.86	0.394	1.55
1-Nov-05	0	6	B	3	1.0005	25	7.847	29.57	0.255	0.96	4.18	15.75	0.243	0.92
1-Nov-05	6	12	B	9	1.0013	25	9.991	41.65	0.400	1.67	6.894	28.74	0.354	1.48
1-Nov-05	6	12	B	9	0.9988	25	8.92	35.76	0.336	1.35	6.009	24.09	0.312	1.25
1-Nov-05	12	18	B	15	0.9941	25	10.47	39.91	0.524	2.00	7.91	30.15	0.605	2.31
1-Nov-05	12	18	B	15	0.9883	25	7.786	31.49	0.376	1.52	5.794	23.44	0.357	1.44
1-Nov-05	18	24	B	21	0.9984	1	128.9	19.75	6.178	0.95	99.21	15.20	7.664	1.17
1-Nov-05	18	24	B	21	0.9949	1	131.5	19.03	8.811	1.28	141.5	20.48	11.02	1.60
1-Nov-05	24	30	B	27	0.9933	1	22.16	3.35	2.742	0.41	23.74	3.59	4.163	0.63
1-Nov-05	24	30	B	27	0.9927	1	18.41	2.93	0.988	0.16	14.02	2.23	1.856	0.29
1-Nov-05	30	36	B	33	0.9932	1	1.875	0.26	0.145	0.02	2.077	0.29	0.191	0.03
1-Nov-05	30	36	B	33	0.9951	1	2.153	0.36	0.219	0.04	3.521	0.59	0.256	0.04

Table A-5b Newport News Metals Extraction Data

Date	Top depth (in)	Botton Depth (in)	Core	Average Depth (in)	Wet Wt. of Sample (g)	Dilution	ICP [Mn2+] (mg/L)	Mn2+ coating (mg/g)	ICP [Fe] (mg/L)	Fe coating (mg/g)	ICP [Al] (mg/L)	Al coating (mg/g)
9-May-06	0	6	A	3	1.5577	25	5.51	33.70	0.25	1.53	4.098	25.06
9-May-06	0	6	A	3	1.6204	25	5.646	33.26	0.234	1.38	3.831	22.57
9-May-06	6	12	A	9	1.5763	25	4.386	24.11	0.209	1.15	3.236	17.79
9-May-06	6	12	A	9	1.62	25	4.259	25.97	0.206	1.26	3.004	18.32
9-May-06	12	18	A	15	1.6333	25	4.709	25.52	0.231	1.25	3.361	18.22
9-May-06	12	18	A	15	1.7774	25	5.162	25.34	0.249	1.22	3.893	19.11
9-May-06	18	24	A	21	1.8773	1	105.9	19.90	6.389	1.20	96.98	18.23
9-May-06	18	24	A	21	1.7251	1	95.2	21.00	5.89	1.30	84.89	18.73
9-May-06	24	30	A	27	1.6103	1	47.23	9.74	4.78	0.99	44.66	9.21
9-May-06	24	30	A	27	1.7451	1	43.75	8.48	3.332	0.65	41.22	7.99
9-May-06	30	36	A	33	1.651	1	12.62	2.11	1.485	0.25	12.05	2.02
9-May-06	30	36	A	33	1.9182	1	18.09	3.49	1.801	0.35	16.4	3.16
9-May-06	0	6	B	3	1.5815	25	5.756	34.87	0.224	1.36	4.051	24.54
9-May-06	0	6	B	3	1.7833	25	7.306	38.92	0.285	1.52	5.174	27.57
9-May-06	6	12	B	9	1.8763	25	5.771	32.71	0.278	1.58	4.138	23.45
9-May-06	6	12	B	9	1.7042	25	4.747	23.33	0.231	1.14	3.553	17.46
9-May-06	12	18	B	15	1.8228	25	4.395	22.01	0.23	1.15	3.288	16.47
9-May-06	12	18	B	15	1.9003	25	5.996	29.73	0.304	1.51	4.528	22.45
9-May-06	18	24	B	21	1.6615	1	82.45	18.47	4.899	1.10	75.4	16.89
9-May-06	18	24	B	21	1.6464	1	77.21	17.62	4.75	1.08	70.86	16.17
9-May-06	24	30	B	27	1.794	1	23.19	4.42	2.505	0.48	23.4	4.46
9-May-06	24	30	B	27	1.5183	1	20.9	4.69	2.021	0.45	21.4	4.80
9-May-06	30	36	B	33	1.82	1	8.283	1.50	1.207	0.22	8.463	1.53
9-May-06	30	36	B	33	1.8464	1	5.31	0.93	1.024	0.18	6.215	1.09

Table A-6 Canteraf Metals Extraction Data

Top depth (in)	Botton Depth (in)	Core	Average Depth (In)	Date	Fluid Amount (L)	Dilution	ICP [Mn2+] (mg/L)	Mn2+ coating (mg/g)	ICP [Fe] (mg/L)	Fe coating (mg/g)	ICP [Al] (mg/L)	Al coating (mg/g)	ICP [Ca] (mg/L)	Ca coating (mg/g)
0	6	1A	3	31-Sep-05	0.25	1	0.253	0.04	20.46	3.57	5.51	0.96	1.881	0.33
0	6	1A	3	31-Sep-05	0.25	1	0.496	0.09	29.56	5.18	5.846	1.02	2.106	0.37
6	12	1A	9	31-Sep-05	0.25	1	0.603	0.11	58.04	10.56	4.485	0.82	2.036	0.37
6	12	1A	9	31-Sep-05	0.25	1	0.216	0.04	36.92	6.20	5.489	0.92	1.765	0.30
12	18	1A	15	31-Sep-05	0.25	1	0.512	0.09	32.17	5.69	3.755	0.66	1.846	0.33
12	18	1A	15	31-Sep-05	0.25	1	0.423	0.07	47.52	8.35	2.555	0.45	2.917	0.51
18	24	1A	21	31-Sep-05	0.25	1	0.416	0.08	32.54	6.01	1.965	0.36	1.768	0.33
18	24	1A	21	31-Sep-05	0.25	1	0.22	0.04	20.27	3.67	2.815	0.51	1.285	0.23
24	30	1A	27	31-Sep-05	0.25	1	0.531	0.10	161.2	29.65	4.269	0.79	2.616	0.48
24	30	1A	27	31-Sep-05	0.25	1	0.246	0.04	25.3	4.23	4.246	0.71	1.649	0.28
0	6	2A	3	31-Sep-05	0.25	50	8.641	72.30	5.513	46.13	0.772	6.46	2.333	19.52
0	6	2A	3	31-Sep-05	0.25	50	6.491	58.03	3.74	33.44	1.08	9.66	1.619	14.48
6	12	2A	9	31-Sep-05	0.25	50	7.006	64.54	4.381	40.36	1.66	15.29	1.656	15.25
6	12	2A	9	31-Sep-05	0.25	50	7.429	67.31	4.632	41.97	0.986	8.93	1.809	16.39
12	18	2A	15	31-Sep-05	0.25	50	7.516	65.43	4.604	40.08	0.719	6.26	1.939	16.88
12	18	2A	15	31-Sep-05	0.25	50	9.349	80.70	5.135	44.33	1.124	9.70	2.155	18.60
18	24	2A	21	31-Sep-05	0.25	50	7.112	57.10	4.355	34.97	0.968	7.77	1.62	13.01
18	24	2A	21	31-Sep-05	0.25	25	16.34	67.08	8.331	34.20	1.3	5.34	3.406	13.98
24	30	2A	27	31-Sep-06	0.25	25	19.14	84.51	10.22	45.13	1.59	7.02	3.815	16.84
24	30	2A	27	31-Sep-05	0.25	25	17.45	78.41	8.661	38.92	1.251	5.62	3.432	15.42
0	6	1B	3	31-Sep-05	0.25	1	0.905	0.15	191.5	31.26	5.343	0.87	2.869	0.47
0	6	1B	3	31-Sep-05	0.25	1	0.325	0.05	38.15	6.19	1.868	0.30	1.678	0.27
6	12	1B	9	31-Sep-05	0.25	1	0.4	0.06	95.51	15.42	3.158	0.51	2.748	0.44
6	12	1B	9	31-Sep-05	0.25	1	0.568	0.09	165.2	27.26	5.207	0.86	3.252	0.54
12	18	1B	15	31-Sep-05	0.25	1	0.685	0.12	271	47.03	7.105	1.23	2.237	0.39
12	18	1B	15	31-Sep-05	0.25	1	0.808	0.13	292.1	48.58	8.785	1.46	4.11	0.68
18	24	1B	21	31-Sep-05	0.25	1	0.703	0.12	270.3	46.69	10.31	1.78	2.839	0.49
18	24	1B	21	31-Sep-05	0.25	1	0.771	0.14	272.7	49.30	10.27	1.86	2.555	0.46
24	30	1B	27	31-Sep-05	0.25	1	0.883	0.16	269.7	48.14	9.824	1.75	2.621	0.47
24	30	1B	27	31-Sep-05	0.25	1	0.879	0.15	296.5	49.94	11.16	1.88	2.567	0.43
0	6	2B	3	31-Sep-05	0.25	25	17.01	76.09	10.89	48.71	1.243	5.56	3.44	15.39
0	6	2B	3	31-Sep-05	0.25	25	18.08	80.03	11.61	51.39	1.668	7.38	3.577	15.83
6	12	2B	9	31-Sep-05	0.25	25	16.42	75.92	11.6	53.63	1.234	5.71	3.163	14.62
6	12	2B	9	31-Sep-05	0.25	25	15.68	65.93	10.49	44.11	1.661	6.98	3.275	13.77
12	18	2B	15	31-Sep-05	0.25	25	5.478	24.83	1.783	8.08	0.304	1.38	1.772	8.03
12	18	2B	15	31-Sep-05	0.25	25	16.25	71.83	10.13	44.78	1.141	5.04	3.204	14.16
18	24	2B	21	31-Sep-05	0.25	25	17.7	78.10	11.56	51.01	1.41	6.22	3.508	15.48
18	24	2B	21	31-Sep-05	0.25	25	18.96	75.67	12.41	49.53	1.503	6.00	3.728	14.88
24	30	2B	27	31-Sep-05	0.25	25	17.46	80.29	10.99	50.54	1.998	9.19	3.718	17.10
24	30	2B	27	31-Sep-05	0.25	25	35.82	154.58	22.22	95.89	3.203	13.82	7.553	32.59

Table A-7 Carno Metals Extraction Data

Top depth (in)	Botton Depth (in)	Core	Average Depth (in)	Date	Fluid Amount (L)	Dilution	ICP [Mn2+] (mg/L)	Mn2+ coating (mg/g)	ICP [Fe] (mg/L)	Fe coating (mg/g)	ICP [Al] (mg/L)	Al coating (mg/g)	ICP [Ca] (mg/L)	Ca coating (mg/g)
UK	Carno	12-Sep-05	6	3	1.8278	1.4737	0.25	1	1.287	0.22	0.028	0.00	11.78	2.00
UK	Carno	12-Sep-05	6	3	1.7179	1.4123	0.25	1	0.637	0.11	0.019	0.00	7.178	1.27
UK	Carno	12-Sep-05	12	9	1.8788	1.5079	0.25	1	1.072	0.18	0.045	0.01	10.51	1.74
UK	Carno	12-Sep-05	12	9	1.7976	1.4428	0.25	1	0.727	0.13	0.012	0.00	15.99	2.77
UK	Carno	12-Sep-05	18	15	1.9572	1.5791	0.25	1	0.694	0.11	0.02	0.00	7.072	1.12
UK	Carno	12-Sep-05	18	15	1.718	1.399	0.25	1	0.699	0.12	0.049	0.01	15.36	2.74
UK	Carno	12-Sep-05	24	21	1.7524	1.4247	0.25	1	0.633	0.11	0.026	0.00	15.61	2.74
UK	Carno	12-Sep-05	24	21	1.8749	1.5207	0.25	1	0.652	0.11	0.029	0.00	17.11	2.81
UK	Carno	12-Sep-05	30	27	1.876	1.4837	0.25	1	0.786	0.13	0.028	0.00	17.39	2.93
UK	Carno	12-Sep-05	30	27	1.801	1.4278	0.25	1	0.598	0.10	0.271	0.05	10.4	1.82
UK	Carno	12-Sep-05	6	3	1.9567	1.5222	0.25	25	29.8	122.36	0.055	0.23	15.66	64.30
UK	Carno	12-Sep-05	6	3	1.8303	1.4334	0.25	25	27.17	118.47	0.054	0.24	14.46	63.05
UK	Carno	12-Sep-05	12	9	1.6371	1.2703	0.25	25	21.66	106.57	0.033	0.16	10.75	52.89
UK	Carno	12-Sep-05	12	9	1.7933	1.4042	0.25	25	26.02	115.81	0.055	0.24	13.45	59.87
UK	Carno	12-Sep-05	18	15	1.9339	1.4843	0.25	25	28.49	119.96	0.049	0.21	15.03	63.29
UK	Carno	12-Sep-05	18	15	1.7907	1.4246	0.25	25	26.22	115.03	0.053	0.23	13.79	60.50
UK	Carno	12-Sep-05	24	21	1.977	1.5334	0.25	25	30.06	122.52	0.063	0.26	16.99	69.25
UK	Carno	12-Sep-05	24	21	1.7877	1.4193	0.25	25	26.87	118.32	0.058	0.26	15.23	67.07
UK	Carno	12-Sep-05	30	27	1.8655	1.4489	0.25	25	28.21	121.69	0.053	0.23	14.7	63.41
UK	Carno	12-Sep-05	30	27	1.6271	1.3088	0.25	25	24.97	119.24	0.251	1.20	13.58	64.85
UK	Carno	12-Sep-05	6	3	1.7458	1.3961	0.25	1	0.935	0.17	0.037	0.01	19.92	3.57
UK	Carno	12-Sep-05	6	3	1.87	1.5426	0.25	1	0.9	0.15	0.025	0.00	17	2.76
UK	Carno	12-Sep-05	12	9	1.6954	1.3549	0.25	1	1.127	0.21	0.047	0.01	14.34	2.65
UK	Carno	12-Sep-05	12	9	1.6695	1.3487	0.25	1	1.633	0.30	0.215	0.04	16.09	2.98
UK	Carno	12-Sep-05	18	15	1.7927	1.4549	0.25	1	0.826	0.14	0.038	0.01	18.43	3.17
UK	Carno	12-Sep-05	18	15	1.8278	1.4858	0.25	1	0.918	0.15	0.031	0.01	15.12	2.54
UK	Carno	12-Sep-05	24	21	1.7428	1.3973	0.25	1	0.563	0.10	0.004	0.00	15.78	2.82
UK	Carno	12-Sep-05	24	21	1.6838	1.3377	0.25	1	0.48	0.09	0.026	0.00	6.087	1.14
UK	Carno	12-Sep-05	30	27	1.7324	1.4281	0.25	1	0.626	0.11	0.024	0.00	15.94	2.79
UK	Carno	12-Sep-05	30	27	1.8197	1.4483	0.25	1	0.884	0.15	0.087	0.02	16.88	2.91
UK	Carno	12-Sep-05	6	3	1.8733	1.4931	0.25	25	28.27	118.34	0.041	0.17	15.18	63.54
UK	Carno	12-Sep-05	6	3	1.8054	1.4464	0.25	25	28.13	121.55	0.057	0.25	15.42	66.63
UK	Carno	12-Sep-05	12	9	1.8715	1.4657	0.25	25	27.81	118.59	0.043	0.18	17.11	72.96
UK	Carno	12-Sep-05	12	9	1.6594	1.3023	0.25	25	23.63	113.41	0.045	0.22	16.4	78.71
UK	Carno	12-Sep-05	18	15	1.6285	1.2594	0.25	25	23.01	114.19	0.05	0.25	11.92	59.16
UK	Carno	12-Sep-05	18	15	1.8565	1.4525	0.25	25	27.01	116.22	0.109	0.47	13.98	60.15
UK	Carno	12-Sep-05	24	21	1.7989	1.4388	0.25	25	28.2	122.50	0.053	0.23	15.36	66.72
UK	Carno	12-Sep-05	24	21	1.8308	1.4639	0.25	25	28.54	121.85	0.045	0.19	16.86	71.98
UK	Carno	12-Sep-05	30	27	1.926	1.4976	0.25	25	44.33	185.00	0.072	0.30	20.69	86.35
UK	Carno	12-Sep-05	30	27	1.844	1.4569	0.25	25	24.69	105.92	0.043	0.18	15.21	65.25

Table A-8 Sobrante Metals Extraction Data

Date	Top depth (in)	Botton Depth (in)	Core	Average Depth (in)	Fluid Amount (L)	Dilution	ICP [Mn2+] (mg/L)	Mn2+ coating (mg/g)	ICP [Fe] (mg/L)	Fe coating (mg/g)	ICP [Al] (mg/L)	Al coating (mg/g)		
1-Jul-05	0	6	A	3	0.25	1	3.998	0.81	1.601	0.32	8.16	1.65		
1-Jul-05	0	6	A	3	0.25	1	3.952	0.84	2.882	0.61	8.609	1.83		
1-Jul-05	6	12	A	9	0.25	1	2.671	0.50	0.991	0.19	5.363	1.01		
1-Jul-05	6	12	A	9	0.25	1	3.082	0.62	2.078	0.42	7.08	1.41		
1-Jul-05	12	18	A	15	0.25	1	2.455	0.51	1.547	0.32	5.31	1.10		
1-Jul-05	12	18	A	15	0.25	1	3.087	0.53	2.324	0.40	6.851	1.19		
1-Jul-05	18	24	A	21	0.25	1	0.714	0.10	2.007	0.28	2.6	0.36		
1-Jul-05	18	24	A	21	0.25	1	0.341	0.06	0.081	0.01	0.838	0.14		
1-Jul-05	24	30	A	27	0.25	1	0.565	0.09	2.606	0.41	2.742	0.43		
1-Jul-05	24	30	A	27	0.25	1	0.532	0.08	1.679	0.25	2.061	0.31		
1-Jul-05	0	6	B	3	0.25	1	2.733	0.51	0.184	0.03	4.34	0.81		
1-Jul-05	0	6	B	3	0.25	1	5.029	0.81	2.455	0.39	9.907	1.59		
1-Jul-05	6	12	B	9	0.25	1	3.479	0.69	2.001	0.40	7.068	1.40		
1-Jul-05	6	12	B	9	0.25	1	2.338	0.46	0.265	0.05	3.842	0.75		
1-Jul-05	12	18	B	15	0.25	1	2.629	0.47	0.66	0.12	4.66	0.84		
1-Jul-05	12	18	B	15	0.25	1	2.264	0.43	0.219	0.04	3.895	0.73		
1-Jul-05	18	24	B	21	0.25	1	1.419	0.23	0.194	0.03	2.549	0.41		
1-Jul-05	18	24	B	21	0.25	1	1.143	0.18	0.121	0.02	2.154	0.34		
1-Jul-05	24	30	B	27	0.25	1	0.848	0.15	2.701	0.47	2.989	0.52		
1-Jul-05	24	30	B	27	0.25	1	0.619	0.11	2.444	0.42	2.587	0.45		

Date	Top depth (in)	Botton Depth (in)	Core	Average Depth (in)	Fluid Amount (L)	Dilution	ICP [Mn2+] (mg/L)	Mn2+ coating (mg/g)	ICP [Fe] (mg/L)	Fe coating (mg/g)	ICP [Al] (mg/L)	Al coating (mg/g)	ICP [Ca] (mg/L)	Ca coating (mg/g)
14-Dec-05	0	5	A	2.5	0.25	1	2.184	0.44	0.227	0.05	4.093	0.82	2.999	0.60
14-Dec-05	0	5	A	2.5	0.25	1	2.339	0.49	0.233	0.05	4.272	0.89	3.145	0.66
14-Dec-05	5	11	A	8	0.25	1	4.189	0.82	3.307	0.65	9.206	1.80	4.947	0.97
14-Dec-05	5	11	A	8	0.25	1	3.644	0.80	2.403	0.53	7.922	1.75	3.68	0.81
14-Dec-05	11	17	A	14	0.25	1	3.568	0.73	2.359	0.48	8.119	1.66	3.861	0.79
14-Dec-05	11	17	A	14	0.25	1	4.094	0.76	2.436	0.45	9.077	1.69	4.648	0.86
14-Dec-05	17	23	A	20	0.25	1	3.178	0.60	4.998	0.95	7.43	1.41	4.124	0.78
14-Dec-05	17	23	A	20	0.25	1	3.021	0.67	2.295	0.51	6.901	1.52	3.725	0.82
14-Dec-05	23	29	A	26	0.25	1	0.885	0.17	4.869	0.91	3.307	0.62	2.357	0.44
14-Dec-05	23	29	A	26	0.25	1	0.733	0.16	3.153	0.67	3.056	0.65	2.509	0.53
14-Dec-05	29	35	A	32	0.25	1	0.49	0.09	1.978	0.35	2.366	0.42	1.701	0.30
14-Dec-05	29	35	A	32	0.25	1	0.721	0.13	3.128	0.55	3.065	0.54	2.193	0.39
14-Dec-05	0	6	B	3	0.25	1	4.827	1.07	1.62	0.36	10.65	2.37	4.933	1.10
14-Dec-05	0	6	B	3	0.25	1	4.923	1.05	1.561	0.33	10.58	2.25	4.395	0.93
14-Dec-05	6	12	B	9	0.25	1	2.714	0.58	2.237	0.48	6.739	1.45	3.951	0.85
14-Dec-05	6	12	B	9	0.25	1	2.943	0.64	2.014	0.44	7.428	1.61	4.695	1.02
14-Dec-05	12	18	B	15	0.25	1	1.297	0.32	0.327	0.08	3.153	0.78	1.781	0.44
14-Dec-05	12	18	B	15	0.25	1	1.69	0.36	2.18	0.47	4.732	1.01	3.611	0.77
14-Dec-05	18	24	B	21	0.25	1	0.898	0.12	3.601	0.49	3.688	0.51	2.684	0.37
14-Dec-05	18	24	B	21	0.25	1	0.485	0.09	2.418	0.45	2.597	0.49	1.757	0.33
14-Dec-05	24	30	B	27	0.25	1	0.604	0.11	2.236	0.40	2.806	0.50	1.709	0.31
14-Dec-05	24	30	B	27	0.25	1	0.48	0.07	0.344	0.05	1.417	0.22	0.958	0.15

Table A-9 USL Metals Extraction Data

Date	Top depth (in)	Botton Depth (in)	Core	Average Depth (in)	Fluid Amount (L)	Dilution	ICP [Mn2+] (mg/L)	Mn2+ coating (mg/g)	ICP [Fe] (mg/L)	Fe coating (mg/g)	ICP [Al] (mg/L)	Al coating (mg/g)
23-Jun-05	0	6	A	3	0.25	1	0.188	0.04	3.657	0.70	2.559	0.49
23-Jun-05	0	6	A	3	0.25	1	0.26	0.05	2.649	0.48	2.749	0.50
23-Jun-05	6	12	A	9	0.25	1	0.221	0.04	3.158	0.61	2.561	0.49
23-Jun-05	6	12	A	9	0.25	1	0.215	0.04	4.263	0.76	2.407	0.43
23-Jun-05	12	18	A	15	0.25	1	0.231	0.05	3.228	0.67	2.317	0.48
23-Jun-05	12	18	A	15	0.25	1	0.219	0.04	2.95	0.55	2.389	0.44
23-Jun-05	18	24	A	21	0.25	1	0.308	0.05	3.502	0.59	3.14	0.53
23-Jun-05	18	24	A	21	0.25	1	0.276	0.05	3.546	0.61	2.99	0.52
23-Jun-05	0	6	B	3	0.25	1	0.24	0.04	6.985	1.09	3.322	0.52
23-Jun-05	0	6	B	3	0.25	1	0.254	0.04	4.83	0.69	3.451	0.50
23-Jun-05	6	12	B	9	0.25	1	0.174	0.03	3.49	0.60	2.599	0.45
23-Jun-05	6	12	B	9	0.25	1	0.132	0.02	2.633	0.43	2.033	0.33
23-Jun-05	12	18	B	15	0.25	1	0.065	0.01	0.353	0.06	0.762	0.13
23-Jun-05	12	18	B	15	0.25	1	0.108	0.02	0.889	0.16	1.218	0.22
23-Jun-05	18	24	B	21	0.25	1	0.187	0.03	1.684	0.30	1.799	0.32
23-Jun-05	18	24	B	21	0.25	1	0.085	0.02	0.473	0.09	0.728	0.14